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Switchable 3D Networks by Light Controlled π-Stacking of Azobenzene Macrocycles

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General Methods

Reagents and Solvents: All chemicals and solvents for reactions were purchased from one of the following commercial sources: Acros, Alfa Aesar, Fluka, Fluorochem, Sigma-Aldrich, Strem or VWR and used without further purification. Dry solvents were either bought in a crown cap flask over molecular sieve or taken from a Pure-SolvTM drying system. THF was predried over $CaCl_2$ and distilled from potassium and benzophenone under nitrogen. For extraction and chromatography technical solvents were redistilled once with a rotatory evaporator prior to usage.

Reactions: All reactions were performed under ambient atmosphere if not stated otherwise. For air sensitive reactions, the solvent was purged by an argon stream and the reaction was done under an argon or nitrogen atmosphere. For moisture sensitive reactions the glass material was heated at 110 °C in a drying oven over night before usage.

Isomerizations: For photochemical isomerisations the azobenzenes the following lamps were used. A handheld 8 Watts 3UV lamp from UVP with switchable wavelengths of 254, 302 and 365 nm, or a 140 W halogen floodlight were taken for the isomerisation. After irradiation analysis by UV-spectroscopy or ^{1}H-NMR spectroscopy were done immediately because of thermal back reaction.

Chromatography: For thin layer chromatography either silica gel 60 F254 glasses with a thickness of 0.25 mm from Merck or Polygram® Alox N/UV254 with a thickness of 0.2 mm from Macherey-Nagel were used. Furthermore, silica gel plates from Whatman (partisil, 250 µm * 20 cm * 20 cm, fluorescent model K6F) were used after cutting them to sizes of 25 * 100 mm for reaction control or 50 * 100 mm for column chromatography control with a glass cutter. Detection was done either by a UV-lamp at 254, 302 or 365 nm or by visualization with vanillin, $KMnO_4$, ninhydrin, iodine or *p*-anisaldehyde. For column chromatography silica gel 60 (40 - 63 µm) from Fluka or neutral aluminium oxide from Merck or Fluka was used. Flash column chromatography was performed under nitrogen pressure.

^{1}H-NMR: For proton nuclear magnetic resonance a Bruker DPX-NMR (400 MHz), Bruker BZH-NMR (250 MHz) or Bruker Avance 500 (500 MHz) instrument was used to measure spectra. Chemical shifts are reported in δ with the unit ppm relative to TMS if possible or otherwise residual solvent peaks. Coupling constants J are reported in Hz. NMR-solvents were bought from Cambridge Isotope Laboratories, Inc. or from ARMAR Ag. Multiplets are written as s for singulet, d for doublet, t for triplet, q for quartet, m for multiplet and bs for broad singulet.

^{13}C-NMR: For carbon nuclear magnetic resonance a Bruker DPX-NMR (100.6 MHz) or a Bruker Avance 500 (125.8 MHz) instrument was used. Chemical shifts are reported in δ with the unit ppm relative to residual solvent peaks.

UV/Vis-Spectroscopy: Absorption spectra throughout the ultraviolet and the visible part of the spectrum were recorded on an Agilent 8453 diode array spectrometer using Hellma quartz cuvettes with a length of 1 cm.

Mass Spectrometry: Electron ionization mass spectrometry (EI-MS) was measured on a VG70-250 mass spectrometer. Fast atom bombardment mass spectrometry (FAB- MS) was measured on a MAR 312 mass spectrometer with 3-nitrobenzyl alcohol or glycine as a matrix and KCl as an additive if necessary. For matrix assisted laser desorption ionization - time of

flight (MALDI-TOF) an Applied Bio Systems Voyager-DeTM instrument was used. The used matrices were 1,8-dihydroxy-10H-anthracen-9-on, 2,6-dihydroxyacetophenone or 2,4,6-trihydroxyacetophenone.

Melting Point: For the melting point measurements a Will Wetzlar or a Büchi 530 instrument were used.

Experimental Procedures

3-Nitro-5-bromobenzoic acid: A flask was charged with 3-nitrobenzoic acid (30.4 g, 180 mmol, 1.00 eq.) and 82 ml of conc. sulphuric acid was added. The solution was heated to 60 °C. Then, NBS (38.8 g, 216 mmol, 1.20 eq.) was added in three portions over 3 h, keeping the temperature between 60 and 70 °C. After complete addition the mixture was stirred over night at 60 °C and poured onto crushed ice (300 g), filtered and washed with water and hexane. The solid was then dissolved in EtOAc (200 ml) and dried over sodium sulphate. The solution was concentrated until a precipitate was observed. Then, hexane was slowly added to crystallize the product out of solution to obtain 36.9 g of a white solid (83 %): mp 160 – 163 °C; ^{1}H NMR (400 MHz, $CDCl_3$, δ): 10.26 (bs, 1H, COOH), 8.88 (s, 1H), 8.64 (s, 1H), 8.57 (s, 1H).
The analytical data corresponded to the literature.[1]

*3-Amino-5-bromobutylbenzoate (**2**):* A solution of 3-nitro-5-bromobenzoic acid (8.11 g, 33.0 mmol, 1.00 eq.) in butanol (60 ml) was cooled to 0 °C. Then, thionyl chloride (3.61 ml, 49.5 mmol, 1.50 eq.) was slowly added drop-wise during 10 min. After that, the mixture was stirred at 100 °C for 3 h and the allowed to cool to rt and 50 ml of water was added. Extraction with ethyl acetate (2x) was followed by washing with sat. aq. $NaHCO_3$ and drying over $MgSO_4$. The solvent was removed under reduced pressure and the residue was dried under high vacuum to obtain 9.50 g of a yellow oil (95 %): ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.79 (s, 1H), 8.56 (s, 1H), 8.49 (s, 1H), 4.42 (t, J = 6.7 Hz, 2H, OCH_2), 1.87 – 1.76 (m, 2H, CH_2), 1.58 – 1.43 (m, 2H, CH_2), 1.02 (t, J = 7.3 Hz, 3H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$, δ): 163.3 (C=O), 148.8, 138.2, 133.7, 130.3, 123.12, 123.05, 66.3 (OCH_2), 30.6 (CH_2), 19.2 (CH_2), 13.7 (CH_3); EI-MS (m/z (%)): 303 (2.6) $[M + 2]^+$, 301 (2.7) $[M^+]$, 56 (100). A flask was charged with 3-nitro-5-bromobutylbenzoate (9.03 g, 29.9 mmol, 1.00 eq.), $SnCl_2$*$2H_2O$ (32.7 g, 145 mmol, 5.00 eq.) and ethanol (60 ml) were added. The mixture was stirred at 60 °C for 3 h and then poured onto 300 g of ice. The mixture was basified with 2 M Na_2CO_3 and extracted with ethyl acetate (3*50 ml). Drying over Na_2SO_4, removal of the solvent and drying under high vacuum, gave 6.36 g of a white solid (78 %): ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.51 (s, 1H), 7.25 (s, 1H), 6.98 (s, 1H), 4.29 (t, J = 6.4 Hz, 2H, OCH_2), 3.85 (bs, 2H, NH_2), 1.76 – 1.69 (m, 2H, CH_2), 1.50 – 1-41 (m, 2H, CH_2), 0.97 (t, J = 7.4 Hz, 3H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$, δ): 166.0 (COOR), 148.1, 133.4, 123.3, 122.6, 122.0, 114.9, 65.6 (OCH_2), 31.1 (CH_2), 19.6 (CH_2), 14.1 (CH_3); EI-MS (m/z (%)): 273 (70) $[M + 2]^+$, 271 (71) $[M^+]$, 215 (100).

*Butyl 3-amino-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate (**4**):* A three necked flask was charged with 3-amino-5-bromobutylbenzoate (**2**) (4.00 g, 14.7 mmol, 1.00 eq.), bis(pinacolato)diboron (**3**) (4.11 g, 16.2 mmol, 1.10 eq.), Pd(dppf)Cl_2*CH_2Cl_2 (960 mg, 8 mol%) and potassium acetate (4.33 g, 44.1 mmol, 3.00 eq.). The flask was flushed with argon for 5 min and dry DMF (80) was added with a syringe. After degassing the mixture with an argon stream for 20 min, the mixture was stirred at 100 °C for 1 h. Then, the reaction mixture was cooled down, diluted with ether (200 ml) and washed with brine and water. Drying over $MgSO_4$, removal of the solvent and flash column chromatography over a short column (silica gel, hexane:EtOAc 2:1) yielded 3.99 g of a pale green oil which solidified upon standing in the fridge for one week (85 %): mp 79 – 81 °C; ^{1}H-NMR: (400 MHz, $CDCl_3$, δ): 7.83 (s, 1H), 7.43 – 7.41 (m, 1H), 7.29 – 7.26 (m, 1H), 4.28 (t, J = 6.8 Hz, 2H, OCH_2), 3.77 (bs, 2H, NH_2), 1.77 – 1.67 (m, 2H, CH_2), 1.49 – 1.39 (m, 2H, CH_2), 1.32 (s, 12H, CH_3), 0.95 (t, J = 7.4 Hz, 3H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$, δ): 167.3 (C=O), 146.4, 131.4, 126.2, 125.8,

111.8, 84.4 (OCH_2, 2C), 65.1 (OCH_2), 31.2 (CH_2), 25.3 (CH_3, 4C) 19.6 (CH_2), 14.2 (CH_3); EI-MS (m/z (%)): 319 (100) [M^+].

*Dibutyl 5,5'-bis[(*E*)-(3-bromophenyl)diazenyl]biphenyl-3,3'-dicarboxylate (**7**):* A flask was charged with butyl 3-amino-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate (**4**) (1.41 g, 4.40 mmol, 1.20 eq.), butyl 3-amino-5-bromobenzoate (**3**) (1.00 g, 3.67 mmol, 1.00 eq.) and $Pd(PPh_3)_4$ (129 mg, 3 mol%) and flushed with argon for 5 min. Then, toluene (110 ml), 1-butanol (8 ml) and 2 M Na_2CO_3 (5 ml) was added. The mixture was degassed with an argon stream for 20 min, heated to 100 °C and stirred at this temperature for 38 h. After mixture had cooled town to room temperature, EtOAc (200 ml) was added and the mixture was washed with brine and water. The organic layer was dried over $MgSO_4$, the solvent was removed under reduced pressure and the residue was purified via flash column chromatography to yield 78 % of a colourless solid (silica gel, hexane:EtOAc 1:1, 1% NEt_3): mp 89 – 93 °C; ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.63 (s, 2H), 7.34 (s, 2H), 7.05 (s, 2H), 4.32 (t, J = 6.7 Hz, 4H, OCH_2), 3.87 (bs, 4H, NH_2), 1.79 – 1.72 (m, 4H, CH_2), 1.52 – 1.43 (m, 4H, CH_2), 0.98 (t, J = 7.4 Hz, 6H, CH_3); ^{13}C NMR: (101 MHz, $CDCl_3$, δ): 167.1 (C=O), 147.2, 142.3, 132.4, 119.0, 118.3, 115.4, 65.3 (OCH_2), 31.2 (CH_2), 19.7 (CH_2), 14.2 (CH_3); EI-MS (m/z (%)): 384 (100) [M^+]. A solution of dibutyl 5,5'-diaminobiphenyl-3,3'-dicarboxylate (**5**) (100 mg, 260 µmol, 1.00 eq.) was treated with 3-bromonitrosobenzene (**6**) (145 mg, 780 µmol, 3.00 eq.). The mixture was stirred at rt over night and the solvent was removed under reduced pressure. Purification by flash column chromatography (silica gel, hexane:DCM 1:1) yielded 136 mg of an orange solid (73 %): ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.61 (s, 2H), 8.52 (s, 2H), 8.43 (s, 2H), 8.14 (s, 2H), 7.97 (d, J = 9.4 Hz, 2H), 7.65 (d, J = 9.4 Hz, 2H), 7.45 (t, J = 9.4 Hz, 2H), 4.44 (t, J = 6.7 Hz, 4H, OCH_2), 1.88 – 1.80 (m, 4H, CH_2), 1.58 – 1.49 (m, 4H, CH_2), 1.02 (t, J = 7.4 Hz, 6H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$, δ): 166.2 (C=O), 153.7, 153.3, 141.2, 134.7, 133.0, 131.1, 131.0, 125.6, 125.3, 124.5, 123.7, 123.7, 66.0 (OCH_2), 31.2 (CH_2), 19.7 (CH_2), 14.2 (CH_3). MALDI-MS (m/z (%)): 719 (100) [M + 1]$^+$, 718 (43) [M^+].

*Dibutyl-5,5'-bis[(*E*)-(3'-amino-5'-(butoxycarbonyl)biphenyl-3yl)diazenyl]biphenyl-3,3'-dicarboxylate:* A flask was charged with dibutyl-5,5'-bis[(*E*)-(3-bromophenyl)diazenyl]biphenyl-3,3'-dicarboxylate (**7**) (818 mg, 1.14 mmol, 1.00 eq.), butyl 3-bromo-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate (**4**) (798 mg, 2.50 mmol, 2.20 eq.) and $Pd(PPh_3)_4$ (80.0 mg, 6 mol%) and degassed by an argon stream for 5 min. Then, THF (75 ml) and 25 ml of a 2 M K_2CO_3 solution was added and the mixture was degassed for 20 min. After stirring for 5 h at 85 °C, the mixture was allowed to cool to rt and the organic layer was collected and washed with brine. The mixture was dried over $MgSO_4$, the solvent was removed and the residue was purified by column chromatography (silica gel, hexane:EtOAc 1:1) to yield an orange oil (1.05 g, 98 %): mp 88 – 92 °C; ^{1}H NMR (400 MHz, $CDCl_3$, δ) 8.63 (s, 2H), 8.52 (s, 2H), 8.47 (s, 2H), 8.22 (s, 2H), 7.99 (d, J = 7.8 Hz, 2H), 7.77 – 7.72 (m, 4H), 7.61 (t, J = 7.8 Hz, 2H), 7.38 (s, 2H), 7.18 (s, 2H), 4.45 (t, J = 6.7 Hz, 4H, OCH_2), 4.34 (t, J = 6.7 Hz, 4H, OCH_2), 3.93 (bs, 4H, NH_2), 1.89 – 1.72 (m, 8H, CH_2), 1.57 – 1.43 (m, 8H, CH_2), 1.05 - 0.95 (m, 12H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$, δ) 166.7 (C=O), 165.93 (C=O), 153.2, 152.8, 147.1, 141.7, 141.6, 140.9, 132.5, 132.2, 130.3, 130.2, 129.6, 125.2, 123.8, 122.4, 121.8, 118.6, 117.8, 115.2, 65.5 (OCH_2), 65.0 (OCH_2), 30.8 (CH_2), 19.3 (CH_2), 13.8 (CH_3); MALDI-MS (m/z (%)): 945 (100) [M^+].

*Macrocycle **1**:* Dibutyl-5,5'-bis[(*E*)-(3'-amino-5'-(butoxycarbonyl)biphenyl-3yl)diazenyl]biphenyl-3,3'-dicarboxylate (973 mg, 1.03 mmol, 1.00 eq.) was dissolved in THF (120 ml) and triethylamine (1.43 ml, 10.3 mmol, 10.0 eq.) was added. Then, lead tetraacetate (3.15 g, 7.11 mmol, 6.9 eq.), dissolved in THF (100 ml) was added drop-wise over 2 min, while stirring. After stirring for 3 h, EDTA (3.01 g, 10.3 mmol, 10.0 eq.), DCM

(50 ml) and water (50 ml) was added and the mixture was rapidly stirred for an additional hour. The organic layer was collected and the aqueous layer was extracted with DCM (50 ml). After washing with brine and drying over $MgSO_4$, the solvent was removed and the residue was purified by flash column chromatography (silica gel, hexane:EtOAc 2:1) to yield an orange solid (463 mg, 48 %): mp > 245 °C; ^{1}H NMR (400 MHz, $CDCl_3$ (c ~ 67 mg/mL), δ): 8.62 – 8.56 (m, 4H), 8.50 (s, 2H), 8.48 – 8.40 (m, 8H), 7.90 – 7.84 (m, 4H), 7.54 (t, J = 7.8 Hz, 2H), 4.48 – 4.38 (m, 8H, OCH_2), 1.91 – 1.83 (m, 8H, CH_2), 1.62 – 1.52 (m, 8H, CH_2), 1.05 (t, J = 7.5 Hz, 12H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$ (c ~ 67 mg/mL), δ): 165.91 (C=O), 165.86 (C=O), 152.9, 152.81, 152.79, 139.9, 139.2, 138.8, 132.6, 132.5, 130.0, 129.4, 129.3, 129.0, 125.5, 125.3, 123.4, 123.0, 122.7, 121.8, 65.53 (OCH_2), 65.51 (OCH_2), 30.86 (CH_2), 30.84 (CH_2), 19.36 (CH_2), 19.34 (CH2), 13.9 (CH_3); MALDI-MS (m/z (%)): 940 (75) [M^+].

Nonyl-3-bromo-5-nitrobenzoate: To a solution of 3-nitro-5-bromocarboxylic acid (6.50 g, 26.4 mmol, 1.00 eq.) in CH_2Cl_2 (100 ml), DMAP (1.61 mg, 13.2 mmol, 0.50 eq.) and 1-nonanol (13.8 ml, 79.2 mmol, 3.00 eq.) were added. The mixture was cooled to 0 °C and DCC (11.4 g, 79.2 mmol, 1.10 eq.) was added in small portions. Then, the mixture was allowed to warm to rt and stirred for 3 h. The precipitate was removed by filtration and the filtrate was concentrated under reduced pressure. The residue was purified by column chromatography (silica gel, hexane:EtOAc 15:1) to yield 8.93 g of a pale yellow oil (91 %): ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.77 (s, 1H), 8.54 (s, 1H), 8.47 (s, 1H), 4.38 (t, J = 6.8 Hz, 2H, OCH_2), 1.83 – 1.76 (m, 2H, CH_2), 1.48 – 1.20 (m, 12H, CH_2), 0.88 (t, J = 7.8 Hz, 3H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$, δ): 163.7 (C=O), 149.2, 138.6, 134.0, 130.7, 123.5, 123.4, 67.0 (OCH_2), 32.2 (CH_2), 29.8 (CH_2), 29.62 (CH_2), 29.61 (CH_2), 29.0 (CH_2), 26.3 (CH_2), 23.1 (CH_2), 14.5 (CH_3); EI-MS (m/z (%)): 373 (1.2) [M + 1]$^+$, 371 (1.2) [M^+], 69 (100).

Nonyl-3-bromo-5-aminobenzoate: A solution of nonyl-3-bromo-5-nitrobenzoate (8.15 g, 21.9 mmol, 1.00 eq.) in acetic acid (40 ml) was heated to 80 °C. Then, iron powder (6.60 g, 118 mmol, 5.40 eq.) was added slowly during 90 min to keep the temperature below 90 °C. After complete addition, the reaction was stirred for additional 30 min, when it was diluted with water (130 ml). After extraction with *tert*BuOMe (2*100 ml), washing of the combined organic phases with water (70 ml) and drying over $MgSO_4$, the solvent was evaporated under reduced pressure to yield 7.49 g of the desired product as a yellow oil (quant): ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.51 (s, 1H), 7.25 (s, 1H), 6.98 (s, 1H), 4.27 (t, J = 6.7 Hz, 2H, OCH_2), 3.84 (bs, 2H, NH_2), 1.77 – 1.70 (m, 2H, CH_2), 1.45 – 1.21 (m, 12H, CH_2), 0.88 (t, J = 7.8 Hz, 3H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$, δ): 166.0 (C=O), 148.1, 133.4, 123.3, 122.6, 122.0, 115.0, 65.9 (OCH_2), 32.3 (CH_2), 29.9 (CH_2), 29.67 (CH_2), 29.64 (CH_2), 29.1 (CH_2), 26.4 (CH_2), 23.1 (CH_2), 14.5 (CH_3).
EI-MS (m/z (%)): 343 (58) [M + 2]$^+$, 341 (59) [M^+], 215 (100).

*Boronic ester **13**:* A three necked flask was charged with nonyl-3-bromo-5-aminobenzoate (3.00 g, 8.76 mmol, 1.00 eq.), Pd(dppf)Cl_2*CH_2Cl_2 (572 mg, 701 µmol, 8 mol%), bis(pinacolato)diboron (**3**) (2.45 g, 9.64 mmol, 1.10 eq.) and potassium acetate (3.00 g, 26.3 mmol, 3.00 eq.). The flask was flushed with argon for 5 min and dry DMF (65 ml) was added with a syringe. After degassing the mixture with an argon stream for 20 min, the mixture was stirred at 100 °C for 1 h. After the reaction mixture was cooled down, it was diluted with ether (250 ml) and washed with brine and water. Drying over $MgSO_4$, removal of the solvent and flash column chromatography over a short column (silica gel, hexane:EtOAc 4:1) yielded 2.70 g a pale green oil (79 %): ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.85 (s, 1H), 7.43 (s, 1H), 6.29 (s, 1H), 4.28 (t, J = 6.8 Hz, 2H, OCH_2), 1.78 – 1.71 (m, 2H, CH_2), 1.46 – 1.22 (m, 24H, CH_2, CH_3), 0.89 – 0.86 (m, 3H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$, δ): 167.3 (C=O), 146.3, 131.5, 126.3, 125.7, 118.8, 110.0, 84.4, 65.5 (OCH_2), 32.6 (CH_2), 29.9 (CH_2), 29.7 (CH_2), 29.6

(CH_2), 29.2 (CH_2), 26.4 (CH_2), 25.3 (CH_3), 23.1 (CH_2), 14.5 (CH_3); EI-MS (m/z (%)): 389 (100) [M^+].

*3-Nitro-5-bromobenzoic alcohol (**12**):* An oven-dried three-necked flask was put under an argon atmosphere and charged with 3-nitro-5-bromobenzoic acid (30.0 g, 122 mmol, 1.00 eq.) and 85 ml of dry THF. The solution was cooled to –15 °C and a 2M BH_3*SMe_2 complex in THF (62.0 ml, 124 mmol, 1.02 eq.) was added drop-wise so that the temperature stayed below –10 °C. After complete addition, the mixture was stirred for one hour at –15 °C, and then for 5 h at 60 °C. The solvent were removed under reduced pressure and the residue was slowly poured onto 200 ml of sat. aq. $NaHCO_3$. The mixture was extracted with EtOAc (3 * 100 ml), washed with water and brine, dried over $MgSO_4$ and concentrated under reduced pressure. The white solid was dried under high vacuum to afford 17.1 g (99 %) of **14** as a white solid: mp 88 °C; ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.28 (s, 1H), 8.17 (s, 1H), 7.86 (s, 1H), 4.82 (s, 2H, CH_2), 2.05 (bs, 1H, OH).
The analytical data corresponded to the literature.[2]

*4-[(Tri*iso*propylsilyl)ethynyl]phenol (**10**):* A flask was charged with 4-iodophenol (**8**) (2.00 g, 9.00 mmol, 1.00 eq.), tri*iso*propylsilylacetylene (**9**) (2.06 ml, 9.00 mmol, 1.00 eq.), $Pd(PPh_3)_4$ (520 mg, 5 mol%) and copper(I) iodide (171 mg, 10 mol%). The flask was flushed with argon and dry THF (60 ml) and diisopropylamine (20 ml) was added. The mixture was degassed by an argon stream for 15 min and then stirred at 70 °C for 2 h. After the solution had cooled down, it was washed with sat. aq. NH_4Cl (2*100 ml) and brine (100 ml). After drying over $MgSO_4$ and removal of the solvent, the residue was purified by flash column chromatography (silica gel, cyclohexane:EtOAc 3:2) to yield 1.98 g of a brown solid (80 %): mp 85 – 88 °C; ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.37 (d, J = 8.6 Hz, 2H), 6.75 (d, J = 8.6 Hz, 2H), 4.87 (bs, 1H, OH), 1.12 [s, 21H, $CH(CH_3)_2$]; ^{13}C NMR (101 MHz, $CDCl_3$, δ): 155.6, 133.7 (2C), 116.1, 115.3 (2C), 106.9 (CC≡C), 88.7 (CC≡C), 18.7 (CH_3), 11.4 (CH);
EI-MS (m/z (%)): 274 (15) [M^+], 231 (100) [$M - C_3H_7]^+$.

*{(4-[(3-Bromo-5-nitrobenzyl)oxy]phenyl)ethynyl}tri*iso*propylsilane:* Triphenylphosphine (1.93 g, 7.36 mmol, 1.00 eq.) was dissolved in 40 ml of dry THF and cooled to 0 °C. To this solution diethyl azo diformate (1.19 ml, 7.36 mmol, 1.00 eq.) was added drop-wise. This mixture was stirred for 30 min at 0 °C and a solution of 3-bromo-5-nitrobenzylic alcohol (**12**) (1.71 g, 7.36 mmol, 1.00 eq.) and 4-[(tri*iso*propylsilyl)ethynyl]phenol (**10**) (2.02 g, 7.36 mmol, 1.00 eq.) in THF (30 ml) was added. The mixture was stirred for 1 h at 0 °C and 16 h at rt. The solvent was removed under reduced pressure and the residue was subjected to flash column chromatography (silica gel, hexane:EtOAc 15:1) to yield 2.70 g of a pale yellow solid (75 %): mp 101 – 104 °C; ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.33 (s, 1H), 8.24 (s, 1H), 7.91 (s, 1H), 7.44 (d, J = 8.8 Hz, 2H), 6.89 (d, J = 8.8 Hz, 2H), 5.13 (s, 2H, CH_2), 1.12 [s, 21H, $CH(CH_3)_2$]; ^{13}C NMR (101 MHz, $CDCl_3$, δ): 157.7, 140.7, 135.8, 133.7 (2C), 126.2, 123.1, 120.7, 117.1 114.6 (2C), 106.6 (CC≡C), 100.0, 89.5 (CC≡C), 68.0 (CH_2), 18.7 (CH_3), 11.4 (CH); EI-MS (m/z (%)): 446 (100) [M + 2 – $C_3H_7]^+$, 444 (95) [$M - C_3H_7]^+$.

*3-Bromo-5-{(4-[(tri*iso*propylsilyl)ethynyl]phenoxy)methyl}aniline:* A flask was charged with {(4-[(3-bromo-5-nitrobenzyl)oxy]phenyl)ethynyl}tri*iso*propylsilane (1.89 g, 3.87 mmol, 1.00 eq.), $SnCl_2$*$2H_2O$ (4.36 g, 19.3 mmol, 5.00 eq.) and ethanol (20 ml) was added. The mixture was stirred at 60 °C for 2 h and then poured onto 300 mg of ice. The mixture was basified with saturated sodium bicarbonat solution and extracted with ethyl acetate (3*40 ml). Drying over Na_2SO_4, removal of the solvent and purification with flash column (silica gel, hexane:EtOAc 3:1) afforded 1.31 g of a yellow oil which solidified upon standing at rt (74 %): mp 71 – 72 °C; ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.40 (d, J = 8.8 Hz, 2H), 6.91 (s, 1H),

6.85 (d, J = 8.8 Hz, 2H), 6.76 (s, 1H), 6.62 (s, 1H), 4.93 (s, 1H, CH_2), 3.74 (bs, 2H, NH_2), 1.12 [s, 21H, $CH(CH_3)_2$]; ^{13}C NMR (101 MHz, $CDCl_3$, δ): 158.5, 148.0, 139.8, 133.6 (2C), 123.2, 120.0, 117.3, 114.7 (2C), 112.2, 107.0 (CC≡C), 88.9 (CC≡C), 69.2 (CH_2), 18.7 (CH_3), 11.4 (CH); EI-MS (m/z (%)): 459 (22) $[M + 2]^+$, 457 (21) $[M^+]$, 416 (100).

*Diamine **14**:* A solution of 3-bromo-5-{[4-(tri*iso*propylsilyl)phenoxy]methyl}aniline (980 mg, 2.25 mmol, 1.10 eq.) and nonyl-3-amino-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate (**13**) (798 mg, 2.05 mmol, 1.00 eq.) in THF (100 ml) and 2 M aq. K_2CO_3 (25 ml) was degassed by an argon stream for 15 min, and $Pd(PPh_3)_4$ (71.1 mg, 3 mol %) were added. The mixture was stirred under an argon atmosphere for 3 h at 65 °C and then allowed to cool down to rt. The organic layer was separated, washed with brine (50 ml), dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by flash column chromatography (silica gel, hexane:EtOAc 1:2) to yield 1.11 g of a pale yellow oil (85 %): ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.62 (s, 1H), 7.41 (d, J = 8.7 Hz, 2H), 7.33 (s, 1H), 7.03 (s, 1H), 6.99 (s, 1H), 6.90 (d, J = 8.7 Hz, 2H), 6.84 (s, 1H), 6.74 (s, 1H), 5.02 (s, 2H, CH_2), 4.30 (t, J = 6.7 Hz, 2H, CH_2), 3.79 (bs, 4H, NH_2), 1.82 – 1.70 (m, 2H, CH_2), 1.49 – 1.20 (m, 12H, CH_2), 1.12 [s, 21H, $CH(CH_3)_2$], 0.87 (t, J = 6.9 Hz, 3H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$, δ): 166.8 (COO), 158.8, 147.0, 146.7, 142.4, 142.1, 138.4, 133.5 (2C), 131.9, 118.8, 117.9, 116.5, 116.1, 114.9, 114.8 (2C), 113.6, 113.2, 107.1 (CC≡C), 88.8 (CC≡C), 70.0 (CH_2), 65.2 (CH_2), 31.9 (CH_2), 29.5 (CH_2), 29.3 (CH_2), 28.8 (CH_2), 26.0 (CH_2), 24.9 (CH_2), 22.7 (CH_2), 18.7 (CH_3), 14.1 (CH_3), 11.4 (CH); EI-MS (m/z (%)): 640 (29) $[M^+]$, 597 (48) $[M - C_3H_7]^+$, 471 (100).

*Nonyl-3',5-bis[(*E*)-(3-bromophenyl)diazenyl]-5'-{(4-[(tri*iso*propylsilyl)ethynyl]phenoxy)-methyl}-[1,1'-biphenyl]-3-carboxylate:* Diamine **14** (784 mg, 1.27 mmol, 1.00 eq.) was dissolved in acetic acid (30 ml) and 3-bromonitrosobenzene (**6**) (945 mg, 5.08 mmol, 4.00 eq.) was added. The mixture was stirred for 3 d at rt. The solvent was removed at reduced pressure and the black residue was purified by flash column chromatography (silica gel, hexane:DCM 2:1) to yield 905 mg of an orange oil (75 %): ^{1}H NMR (400 MHz, CDCl3, δ): 8.58 (s, 1H), 8.49 (s, 1H), 8.40 (s, 1H), 8.23 (s, 1H), 8.12 (d, J = 6.7 Hz, 2H), 8.04 (s, 1H), 7.94 (t, J = 8.1 Hz, 2H), 7.90 (s, 1H), 7.63 (t, J = 7.0 Hz, 2H), 7.48 – 7.40 (m, 4H), 6.97 (d, J = 8.9 Hz, 2H), 5.25 (s, 2H, CH_2), 4.42 (t, J = 6.8 Hz, 2H, CH_2), 1.89 – 1.80 (m, 2H, CH_2), 1.53 – 1.21 (m, 12H, CH_2), 1.12 [s, 21H, $CH(CH_3)_2$], 0.93 – 0.82 (m, 3H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$, δ): 165.9 (COO), 158.5, 153.4, 153.3, 153.1, 152.8, 141.3, 140.9, 138.9, 134.2, 134.0, 133.7 (2C), 132.5, 130.7, 130.6, 130.5, 128.8, 125.3, 124.8, 123.7, 123.31, 123.26, 123.24, 123.20, 121.8, 121.4, 116.5, 114.8 (2C), 106.9 (CC≡C), 89.0 (CC≡C), 69.4 (CH_2), 65.8 (CH_2), 31.9 (CH_2), 31.6 (CH_2), 29.5 (CH_2), 29.3 (CH_2), 28.8 (CH_2), 26.0 (CH_2), 22.7 (CH_2), 18.7 (CH_3), 14.1 (CH_3), 11.4 (CH); MALDI-MS (m/z (%)): 978.1 (92) $[M + 2]^+$, 977 (100) $[M + 1]^+$, 976 (58) $[M^+]$.

*([(Tri*iso*propylsilyl)ethynyl]phenoxy)methyl-macrocycle:* A solution of nonyl-3',5-bis[(*E*)-(3-bromophenyl)diazenyl]-5'-{(4-[(tri*iso*propylsilyl)ethynyl]phenoxy)methyl}-[1,1'-biphenyl]-3-carboxylate (809 mg, 849 µmol, 1.00 eq.) and nonyl-3-amino-5-(4,4,5,5- tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate (**13**) (826 mg, 2.12 mmol, 2.50 eq.) in THF (50 ml) and 2 M aq. K_2CO_3 (12 ml) was degassed by an argon stream for 15 min, and $Pd(PPh_3)_4$ (58.9 mg, 3 mol %) were added. The mixture was stirred under an argon atmosphere for 18 h at 65 °C and then allowed to cool down to rt. The organic layer was separated, washed with brine (20 ml), dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by flash column chromatography (silica gel, hexane:EtOAc 2:3) to yield 1.18 g of 147 as a pale yellow oil which was used directly in the next step in spite of small impurities (quant.): ^{1}H NMR: (400 MHz, $CDCl_3$, δ): 8.62 (s, 1H), 8.51 (s, 1H), 8.47 (s, 1H), 8.29 (s, 1H), 8.22 (s, 1H), 8.21

(s, 1H), 8.08 (s, 1H), 7.98 (t, J = 8.1 Hz, 2H), 7.92 (s, 1H), 7.79 – 7.72 (m, 4H), 7.61 (td, J = 7.8 Hz, J = 3.0 Hz, 2H), 7.45 (d, J = 8.8 Hz, 2H), 7.38 (s, 2H), 7.18 (s, 2H), 6.98 (d, J = 8.9 Hz, 2H), 5.27 (s, 2H, CH_2), 4.42 (t, J = 6.8 Hz, 2H, CH_2), 4.32 (t, J = 6.4 Hz, 4H, CH_2), 4.21 (bs, 4H, NH_2), 1.90 – 1.72 (m, 6H, CH_2), 1.53 – 1.18 (m, 36H, CH_2), 1.12 [s, 21H, $CH(CH_3)_2$], 0.90 – 0.81 (m, 9H, CH_3). To a solution of the diamine (1.11 g, 826 µmol, 1.00 eq.) in THF (80 ml) and triethylamine (1.15 ml, 8.26 mmol, 10.0 eq.), a suspension of $Pb(OAc)_4$ (2.53 g, 5.70 mmol, 6.90 eq.) in THF (140 ml) was added drop-wise over 20 min. After stirring for additional 3 h, EDTA (2.41 g, 8.26 mmol, 10.0 eq.) was added and 70 ml of water and DCM was added. After stirring for 5 min, The organic layer was separated and the aqueous layer was extracted with DCM (2*15 ml). The combined organic layers were dried over $MgSO_4$ and the solvent was removed under reduced pressure. The dark residue was purified by column chromatography (silica gel, toluene) to yield 588 mg of an orange solid (53 %): mp 146 – 148 °C; ^{1}H NMR: (400 MHz, $CDCl_3$ (c ~ 50 mg/ml), δ): 8.77 – 8.72 (m, 3H), 8.61 – 8.58 (m, 2H), 8.58 – 8.53 (m, 7H), 8.01 – 7.93 (m, 6H), 7.63 (t, J = 7.8 Hz, 2H), 7.48 (d, J = 8.8 Hz, 2H), 7.00 (d, J = 8.8 Hz, 2H), 5.22 (s, 2H, CH_2), 4.43 (t, J = 6.7 Hz, 6H, CH_2), 1.92 – 1.82 (m, 6H, CH_2), 1.56 – 1.24 (m, 36H, CH_2), 1.13 [s, 21H, $CH(CH_3)_2$], 0.91 – 0.85 (m, 9H, CH_3); ^{13}C NMR: (101 MHz, $CDCl_3$ (c ~ 50 mg/ml), δ): 165.94 (COO, 2C), 165.91 (COO), 158.5, 153.1, 152.91, 152.92, 152.84, 152.82, 152.80, 140.0, 139.9, 139.6, 139.2, 138.84, 138.80, 138.7, 133.7 (2C), 132.5, 132.4 (2C), 130.0 (2C), 129.42, 129.40, 129.2, 129.0, 128.8, 127.3, 126.1, 124.9, 124.8, 123.7, 123.6, 123.3, 122.6, 122.4, 121.97, 121.95, 121.0, 120.7, 116.5, 114.8 (2C), 107.0 (CC≡C), 89.0 (CC≡C), 69.5 (CH_2), 65.8 (CH_2), 31.9 (CH_2), 29.6 (CH_2), 29.4 (CH_2), 29.3 (CH_2), 28.8 (CH_2), 26.1 (CH_2), 22.7 (CH_2), 18.7 (CH_3), 14.1 (CH_3), 11.4 (CH); MALDI-MS (m/z (%)):1340 (100) $[M + 2]^+$, 1338 (68) $[M^+]$.

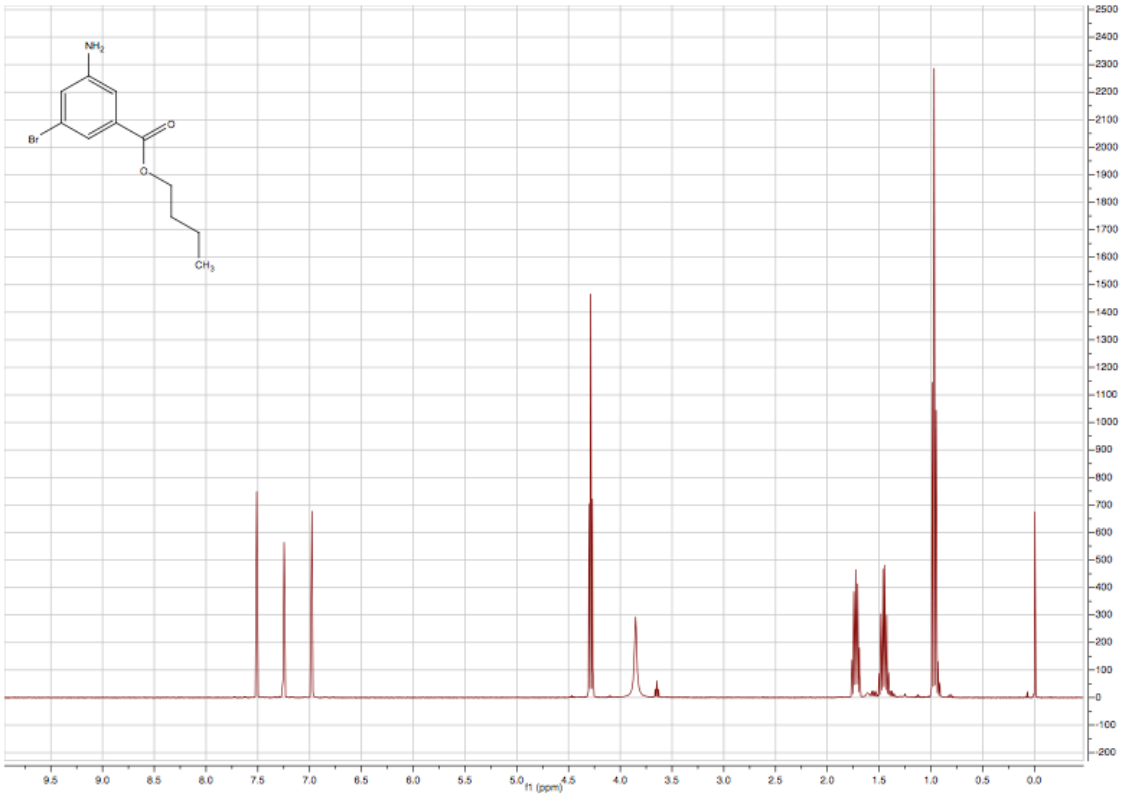
Macrocycle **15**: ([(Tri*iso*propylsilyl)ethynyl]phenoxy)methyl-macrocycle (100 mg, 89.8 µmol, 1.00 eq.) was dissolved in THF (5 ml) and cooled to 0 °C. Then, a 1M solution of TBAF in THF (216 µl, 216 µmol, 2.40 eq.) was added drop-wise, and the mixture was stirred for 19 h at rt. The reaction was quenched by the addition of 25 ml of sat. aq. $NaHCO_3$. The orange precipitate was collected by filtration and washed with water and hexane. After drying under high vacuum, 71 mg of an orange solid was obtained (99 %): mp 183 – 185 °C; ^{1}H NMR (400 MHz, $CDCl_3$ (c ~ 50 mg/ml), δ): 8.75 – 8.68 (m, 6H), 8.09 – 7.94 (m, 12H), 7.71 – 7.64 (m, 4H), 7.51 – 7.46 (m, 4H), 7.04 – 7.00 (m, 4H), 5.29 (s, 4H, CH_2), 4.42 – 4.37 (m, 6H, OCH_2), 3.02 (s, 1H, CH), 1.91 – 1.82 (m, 6H, CH_2), 1.56 – 1.28 (m, 36H, CH_2), 0.90 (t, J = 6.4 Hz, 9H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$ (c ~ 50 mg/ml), δ): 165.92 (COO, 2C), 165.89 (COO), 158.9, 153.1, 152.91, 152.88, 152.82, 152.80, 152.78, 140.0, 139.9, 139.6, 139.2, 138.79, 138.72, 138.69, 133.8 (2C), 132.5, 132.4 (2C), 130.0 (2C), 129.41, 129.39, 129.1, 129.0, 128.8, 127.3, 126.1, 124.9, 124.8, 123.8, 123.6, 123.2, 122.6, 122.4, 122.0, 121.94, 121.0, 120.7, 114.88 (2C), 114.86, 100.0 (CC≡C), 83.5 (CC≡C), 76.1 (CH_2), 69.5 (CH_2), 65.81 (CH_2), 65.79 (CH_2), 31.9 (CH_2), 29.6 (CH_2), 29.4 (CH_2), 29.3 (CH_2), 28.8 (CH_2), 26.1 (CH_2), 22.7 (CH_2), 14.1 (CH_3); MALDI-MS (m/z (%)): 1181 (83) $[M^+]$, 1180 (100).

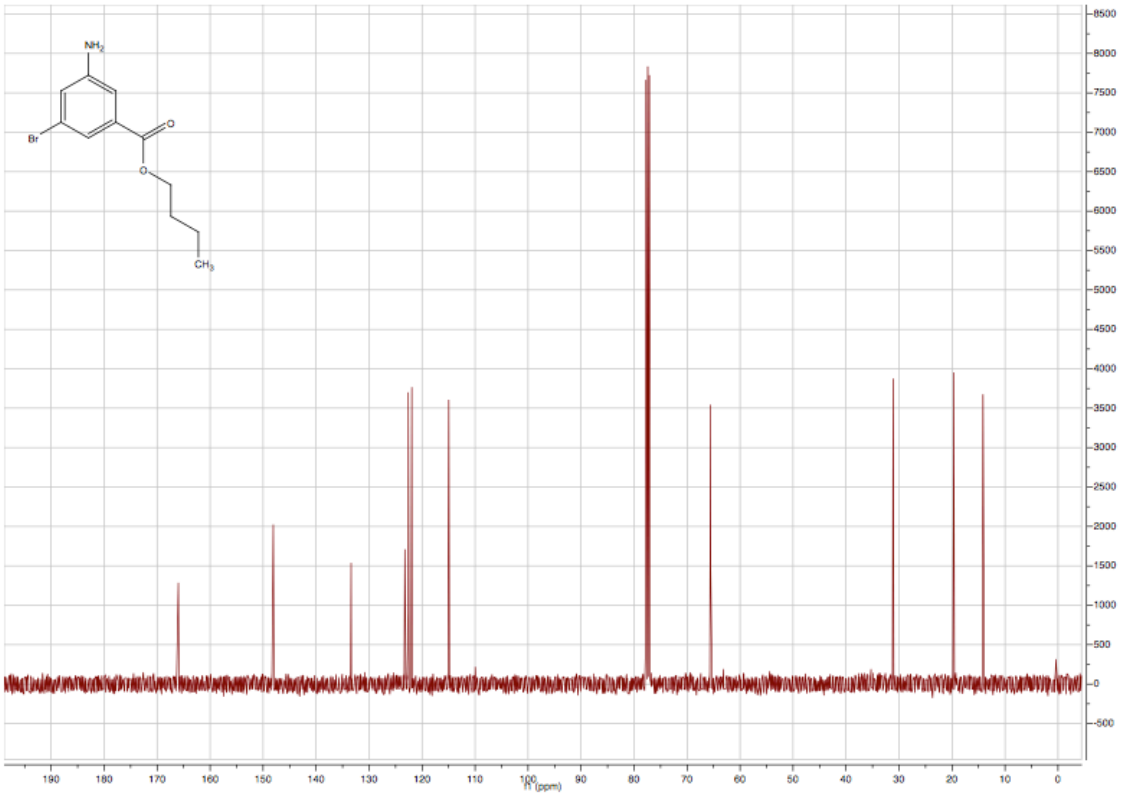
*9,10-(Diazidomethyl)anthracene (**16**):* A solution of 9,10-(dibromomethyl)anthracene[3] (502 mg, 1.38 mmol, 1.00 eq.) in DMF was treated with sodium azide (906 mg, 13.8 mmol, 10.0 eq.) and stirred at 70 °C for 3 d. Then, the solvent was removed under reduced pressure and the residue was purified by flash column chromatography (silica gel, hexane:EtOAc 15:1) to yield 304 mg of yellow crystals (76 %): mp > 150 °C (decomposition); ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.40 – 8.35 (m, 4H), 7.67 – 7.62 (m, 4H), 5.36 (s, 4H, CH_2); ^{13}C NMR: (101 MHz, $CDCl_3$, δ): 130.4, 128.2, 126.7, 124.5 (2C), 46.5; EI-MS (m/z (%)): 288 (64) $[M^+]$, 218 (100).

*Bismacrocycle **17**:* A flask was charged with macrocycle **15** (50.0 mg, 42.3 µmol, 2.00 eq.), 9,10-(diazidomethyl)anthracene (**16**) (6.10 mg, 21.1 µmol, 1.00 eq.), DBU (16.1 µl, 106 µmol, 5.00 eq.) and toluene (20 ml). The solution was degassed by an argon stream for 15 min and CuI (1.2 mg, 30 mol%) was added under argon backflow. After stirring at 70 °C for 20 h, the mixture was allowed to cooled down. Then, it was washed with 1 M aq. HCl (2*20 ml) and water (20 ml). The organic layer was dried over $MgSO_4$ and the solvent was removed under reduced pressure. The residue was dissolved in a small amount of THF and precipitated in cold hexane (150 ml). After standing in the fridge for 5 h, the precipitate was collected by filtration to yield 18 mg of orange flakes (32 %). Another 40 mg (72 %) fraction containing small amounts of impurities could be obtained as an orange gel by removing the solvent from the filtrate and drying under high vacuum: mp > 245 °C; ^{1}H NMR (400 MHz, $CDCl_3$ (c ~ 8 mg/ml), δ): 8.74 – 8.66 (m, 6H), 8.59 – 8.47 (m, 18H), 7.99 – 7.85 (m, 12H), 7.73 - 766 (m, 4H), 7.65 – 7.52 (m, 8H), 7.20 (s, 2H, H-triazene), 7.00 (d, J = 8.5 Hz, 4H), 6.63 (d, 4H, CH_2), 5.17 (s, 4H, CH_2), 4.48 – 4.32 (m, 12H, CH_2), 1.93 – 1.77 (m, 12H, CH_2), 1.66 – 1.19 (m, 72H, CH_2), 0.93 – 0.81 (m, 18H, CH_3); MALDI-MS (m/z (%)): 2650 (100) [M^+].

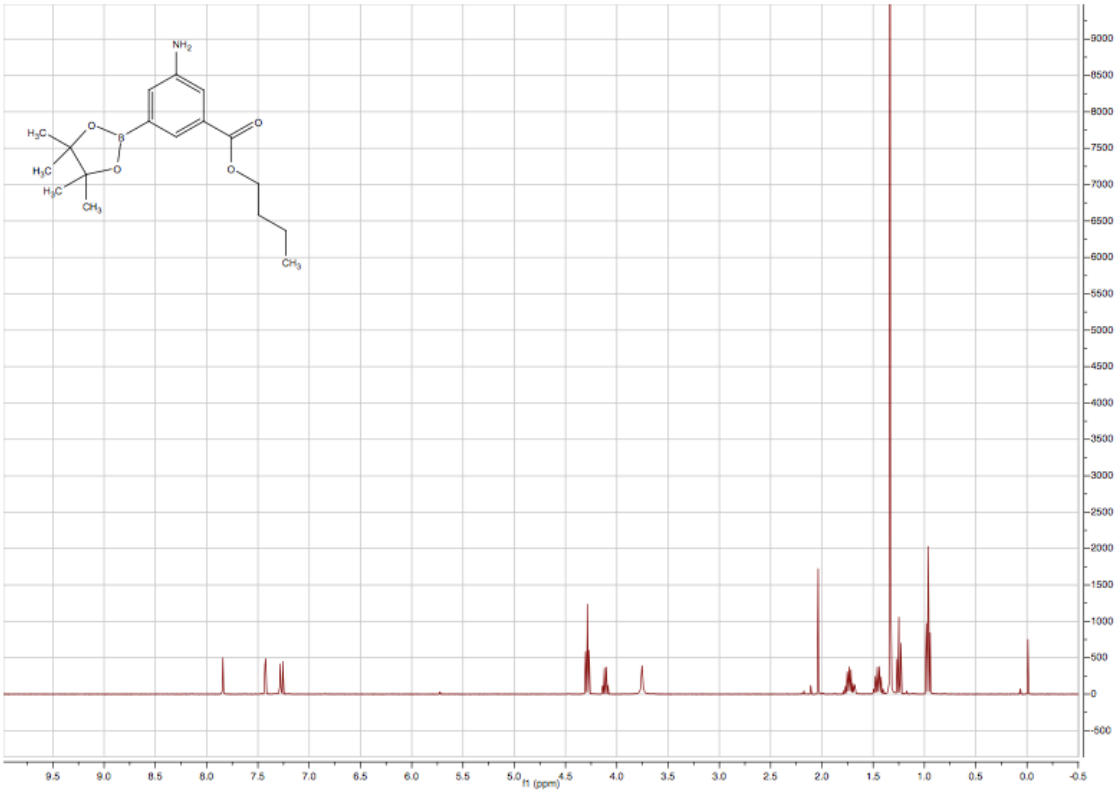
NMR-Spectra

*3-Amino-5-bromobutylbenzoate (**2**)*

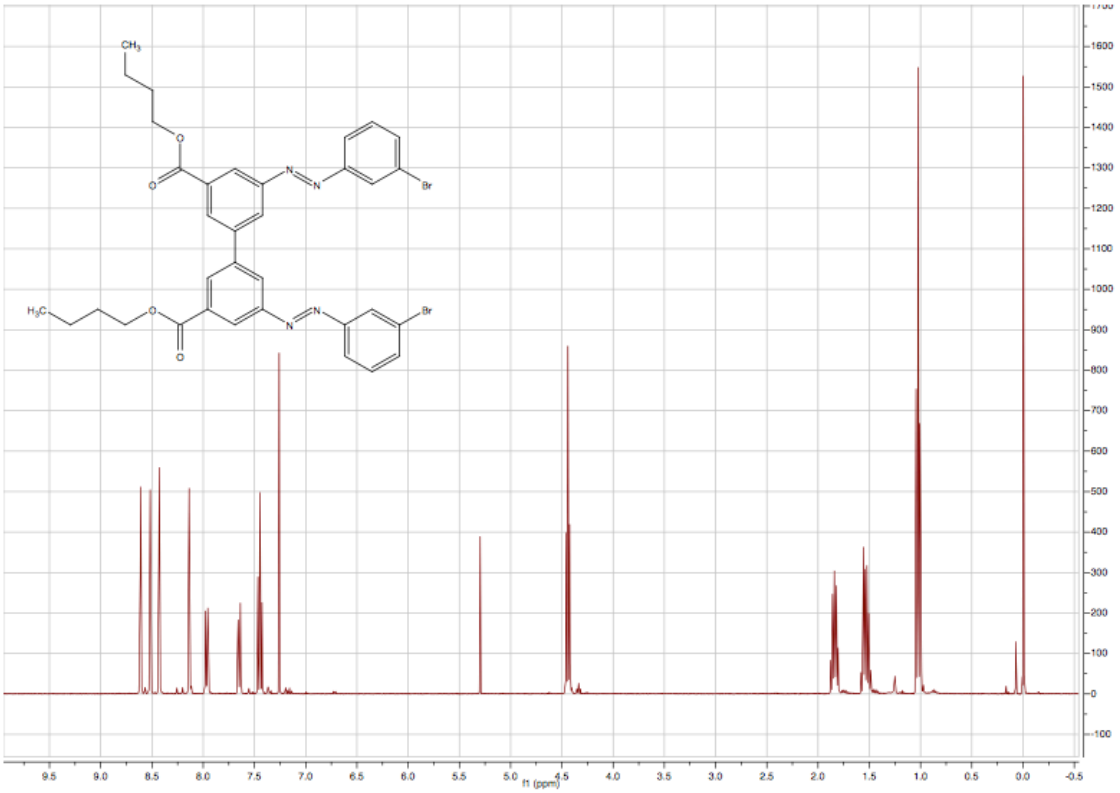


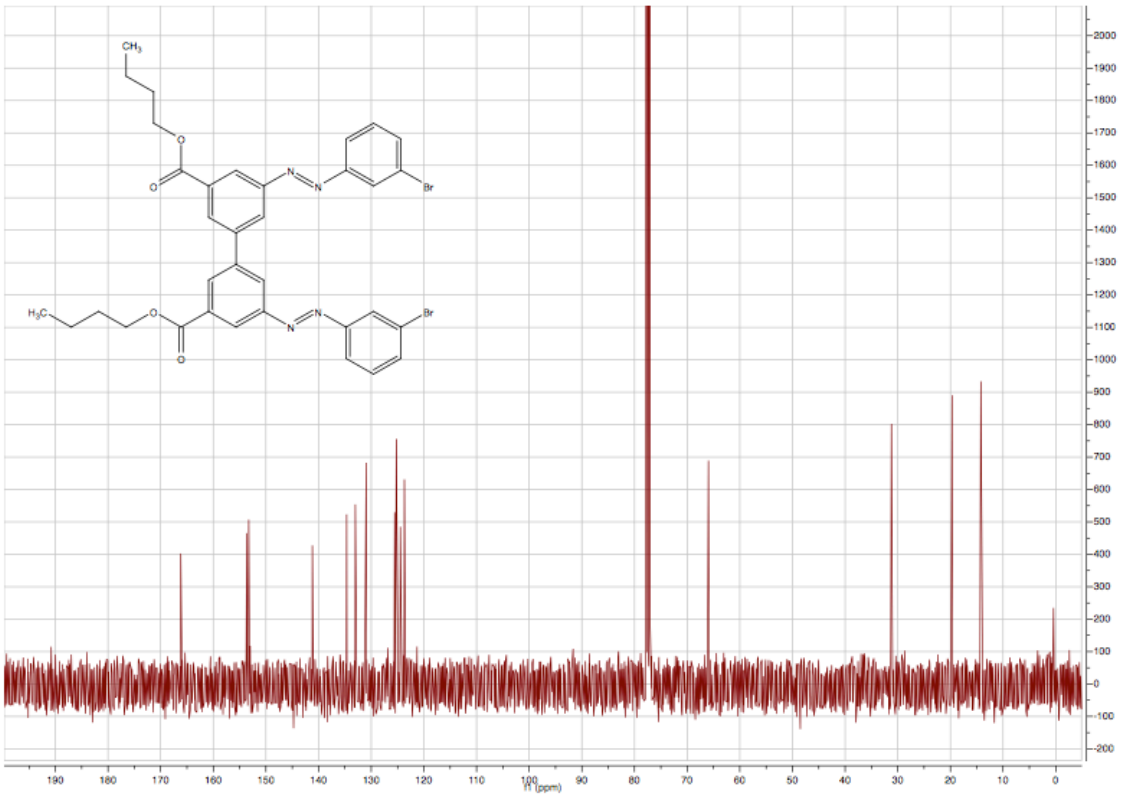


*Butyl-3-amino-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate (**4**)*

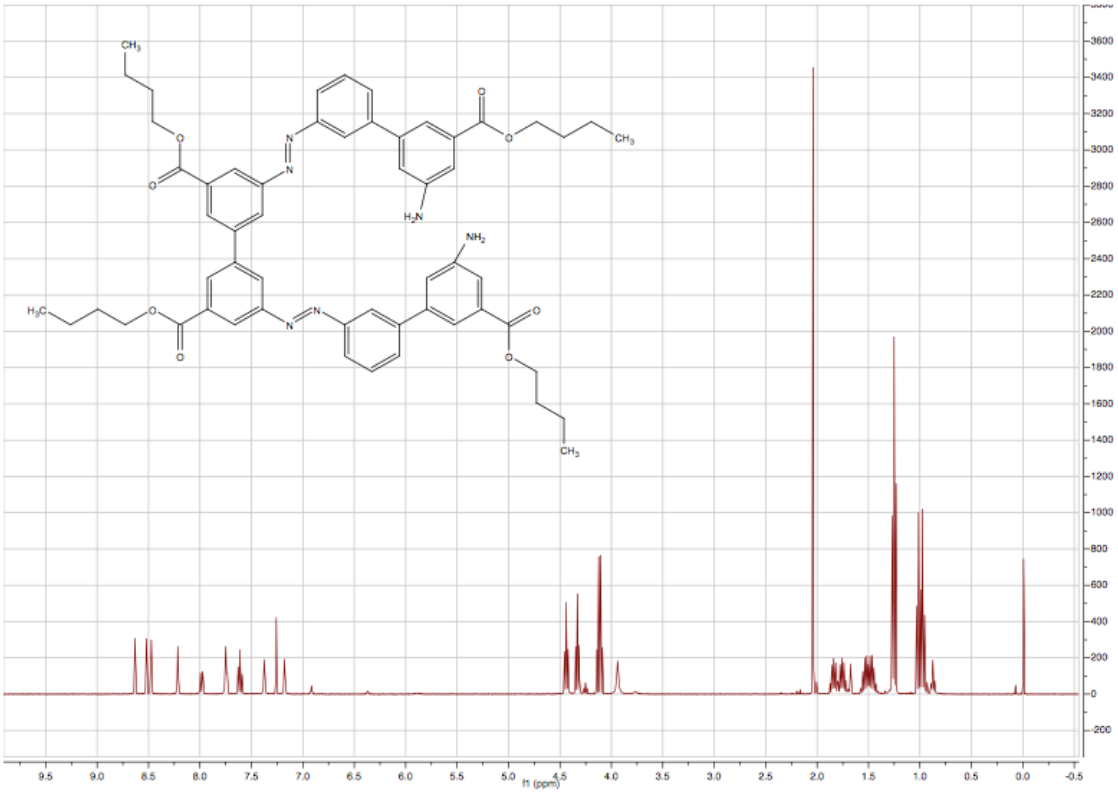


Dibutyl-5,5'-bis[(E)-(3-bromophenyl)diazenyl]biphenyl-3,3'-dicarboxylate (7)

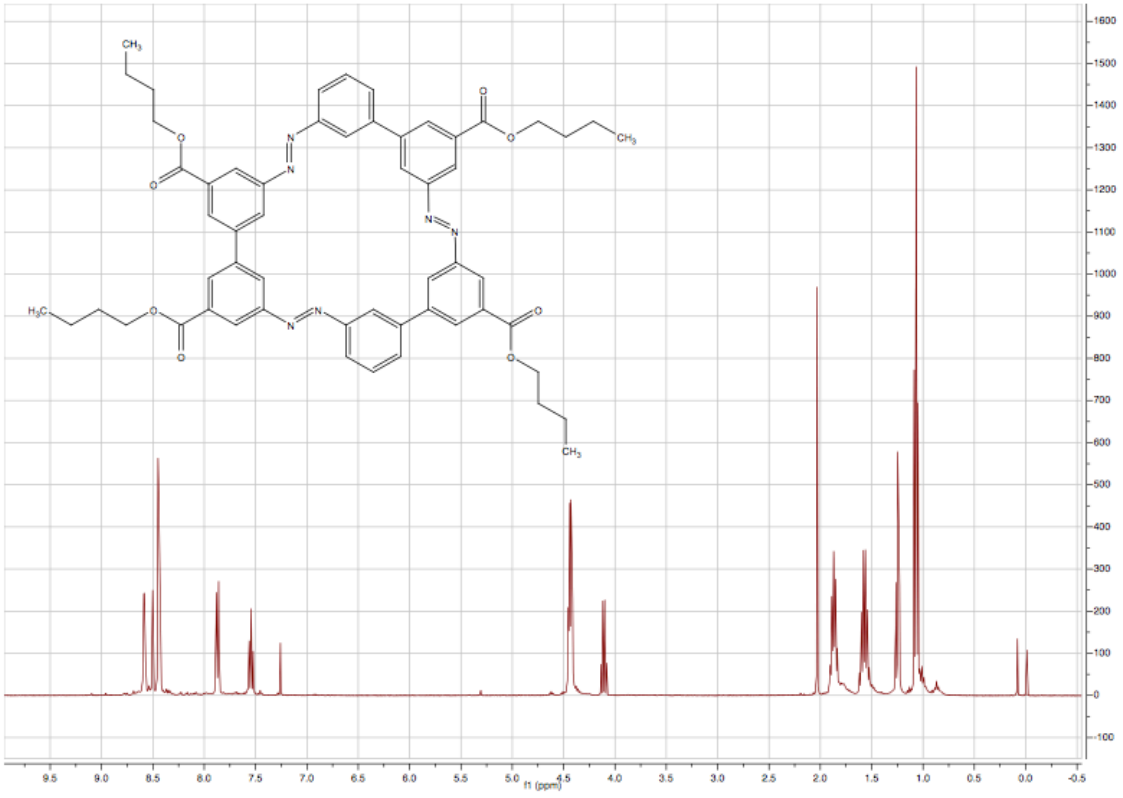


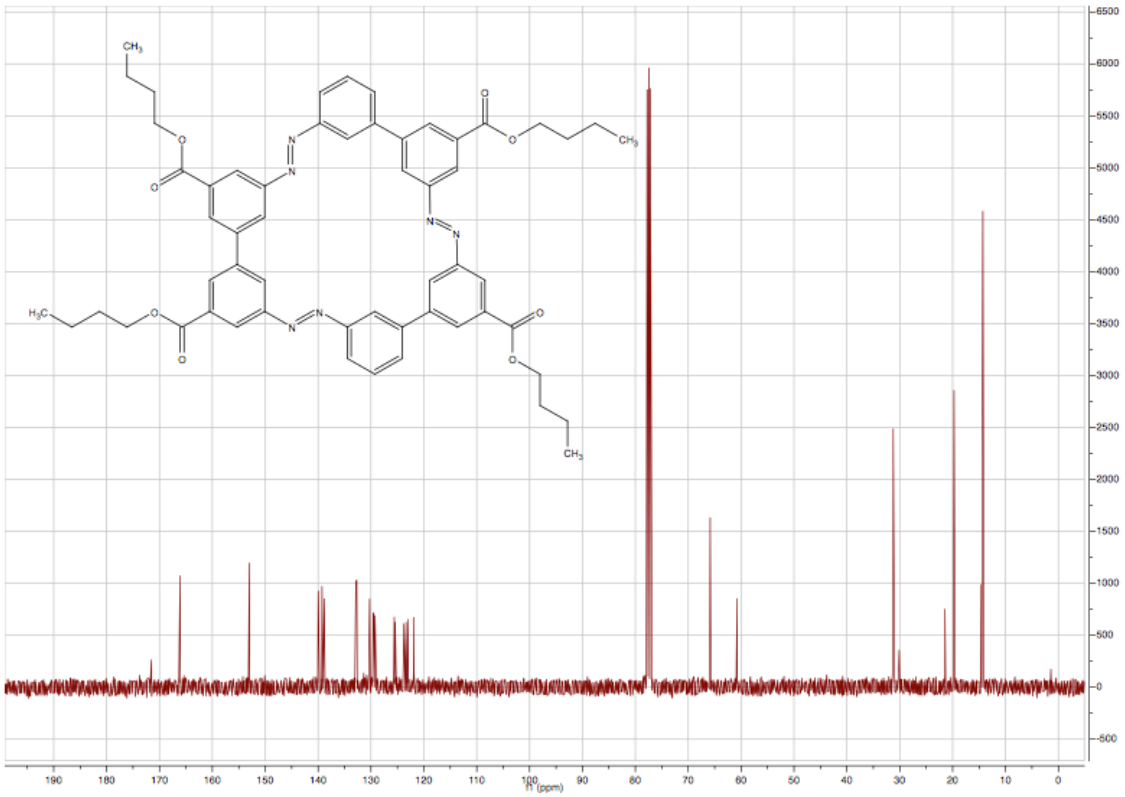


*Dibutyl-5,5'-bis[(*E*)-(3'-amino-5'-(butoxycarbonyl)biphenyl-3yl)diazenyl]biphenyl-3,3'-dicarboxylate*

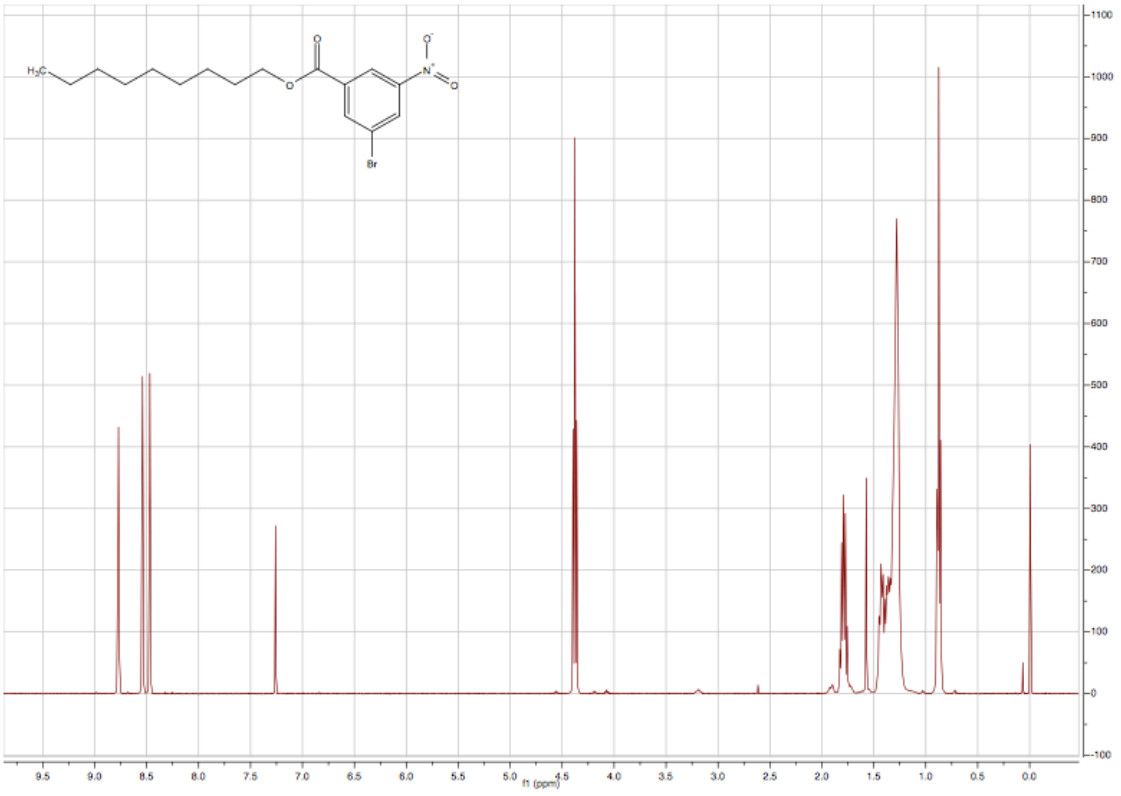


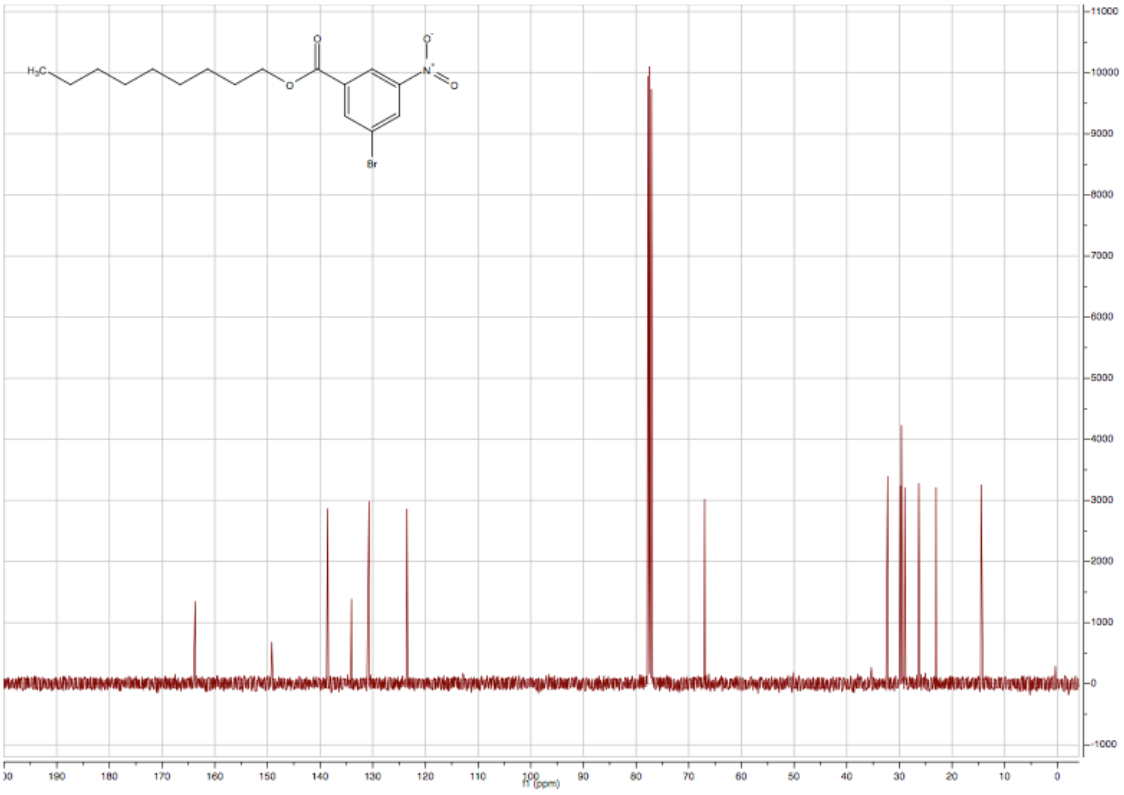
*Macrocycle **1***



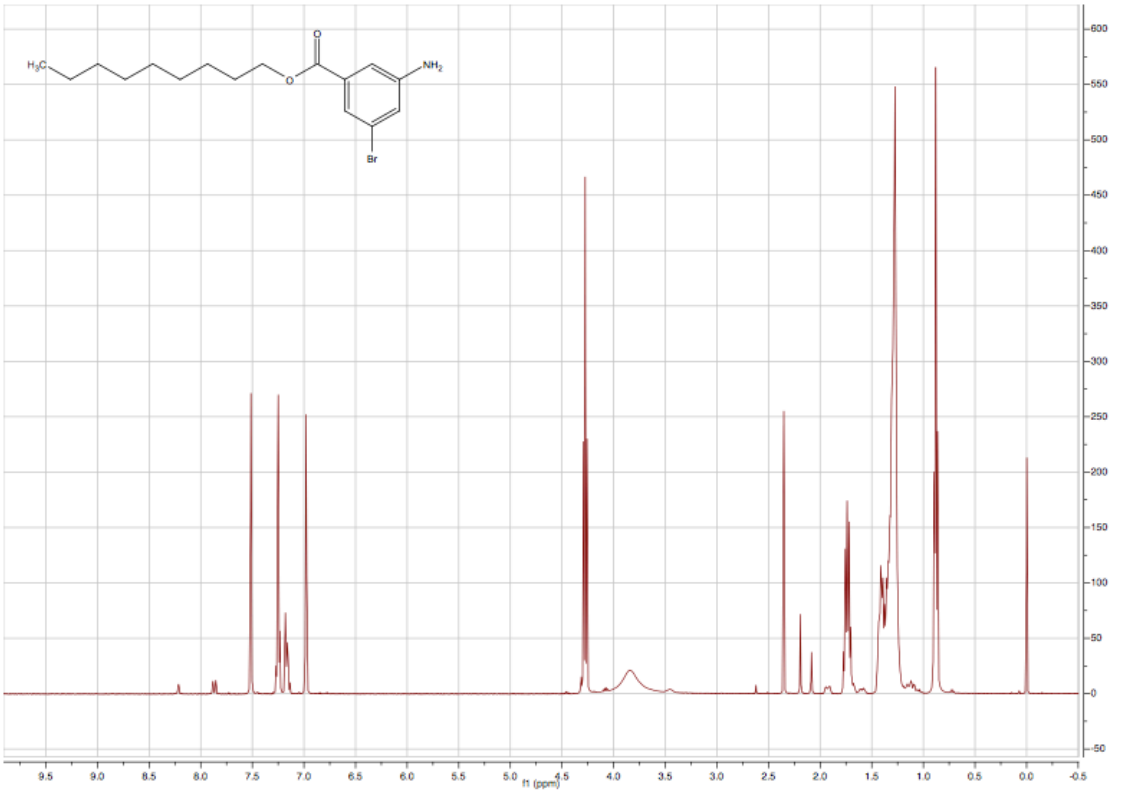


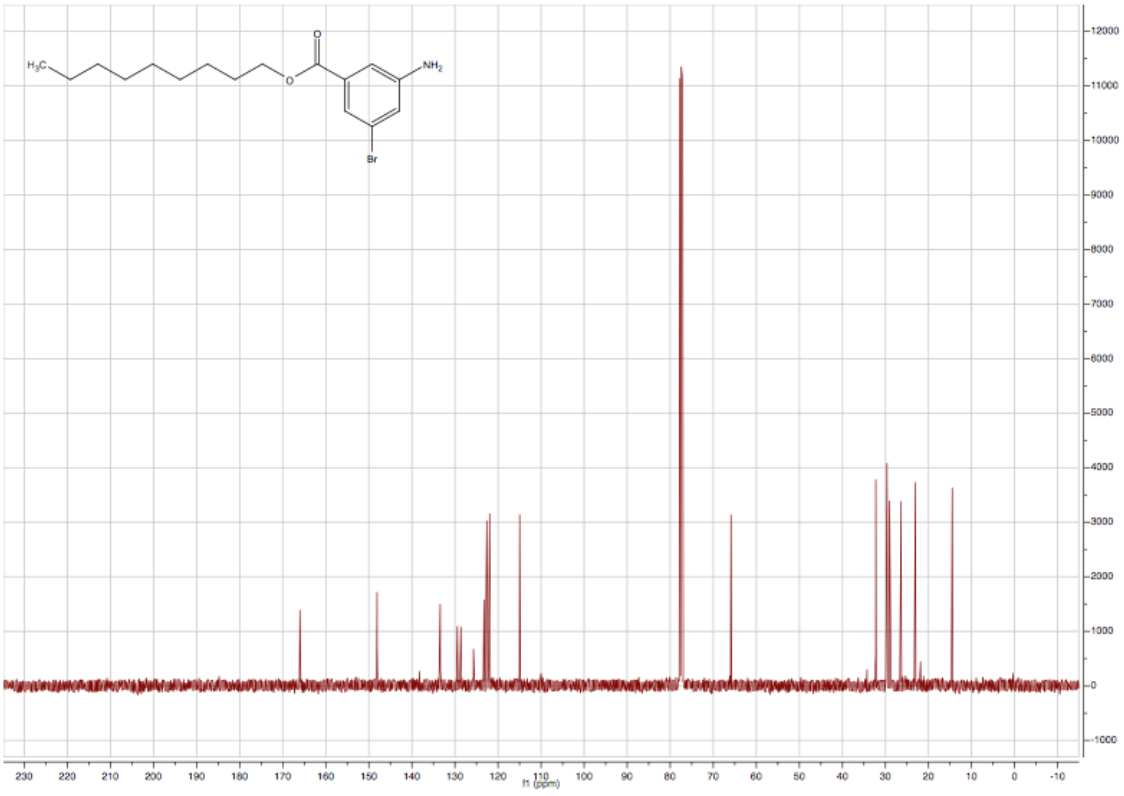
Nonyl-3-bromo-5-nitrobenzoate



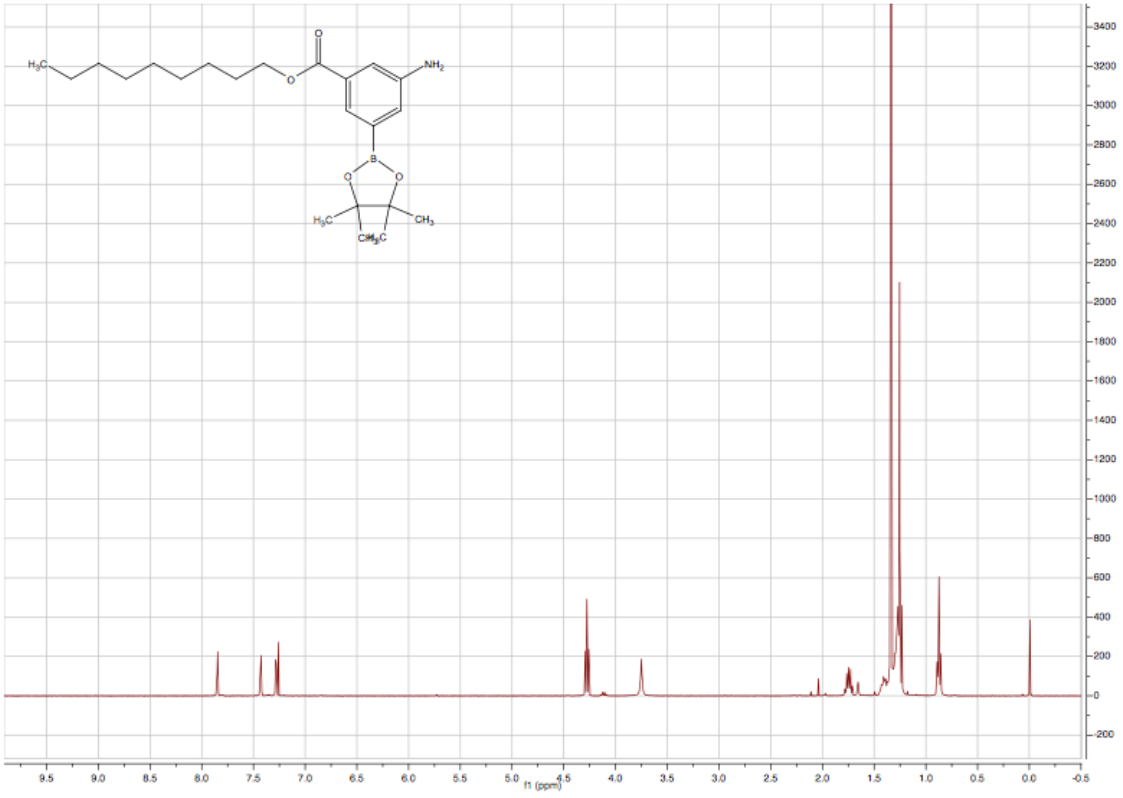


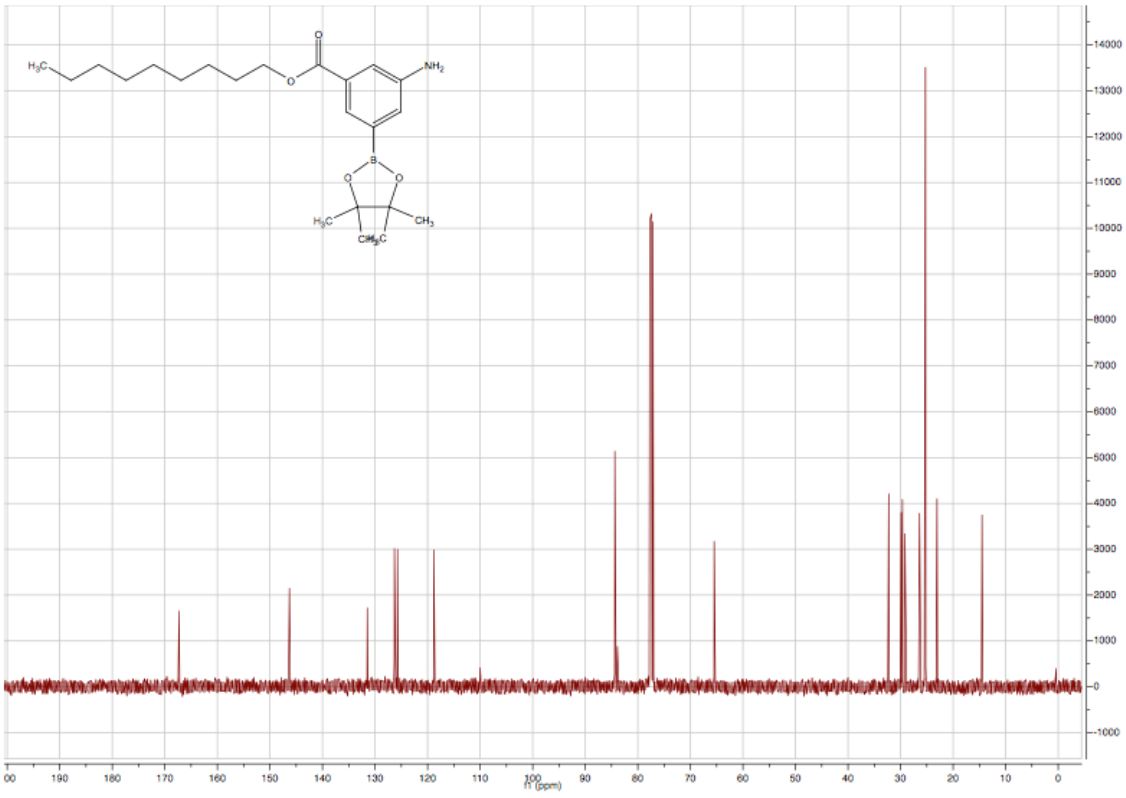
Nonyl-3-bromo-5-aminobenzoate



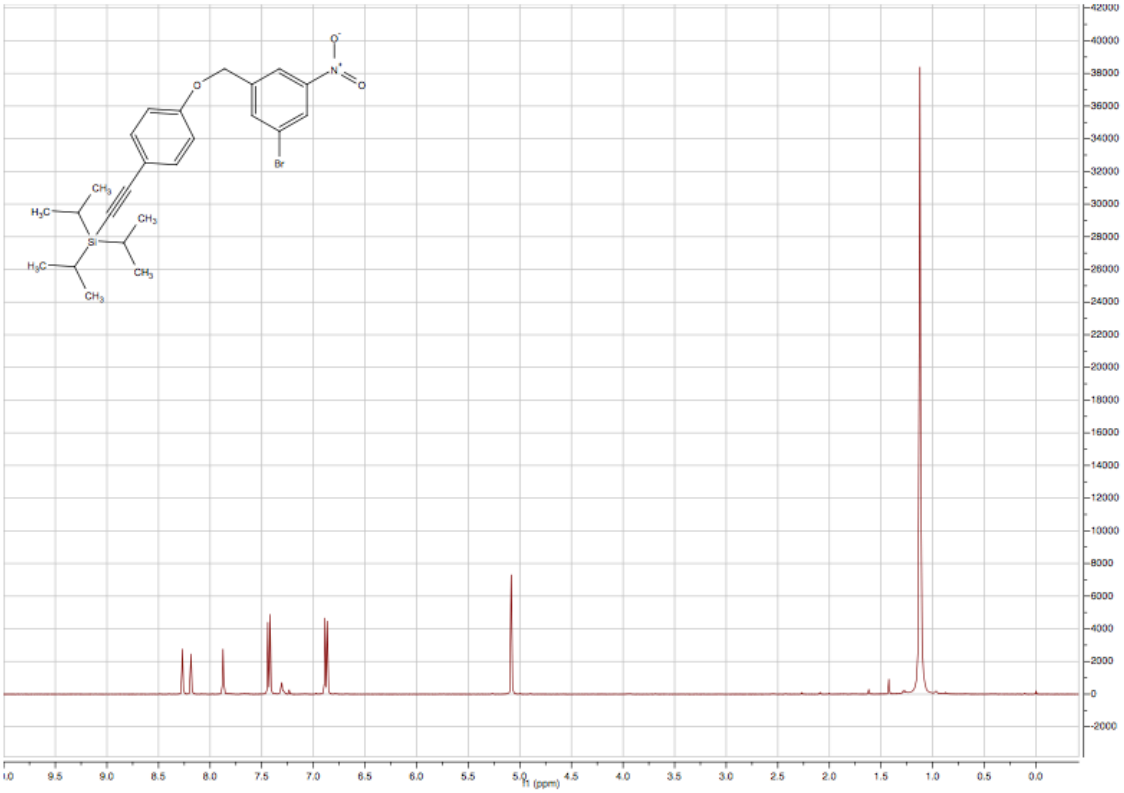


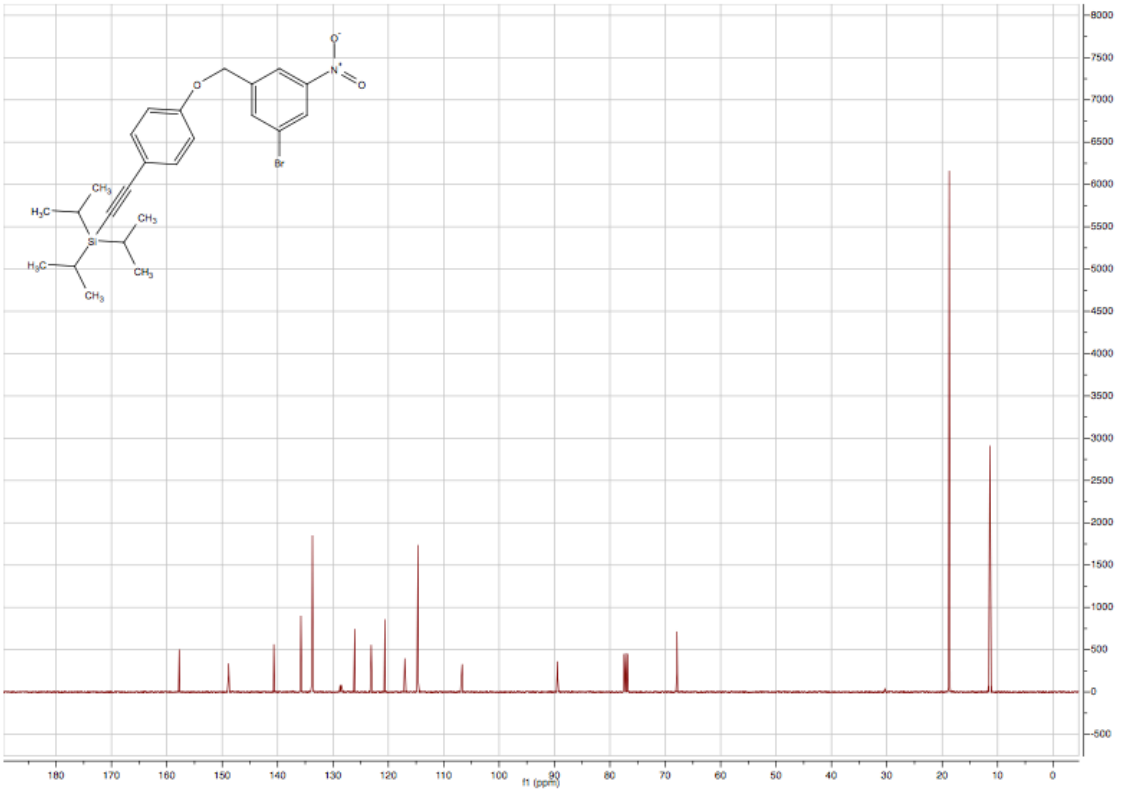
Boronic ester ***13***



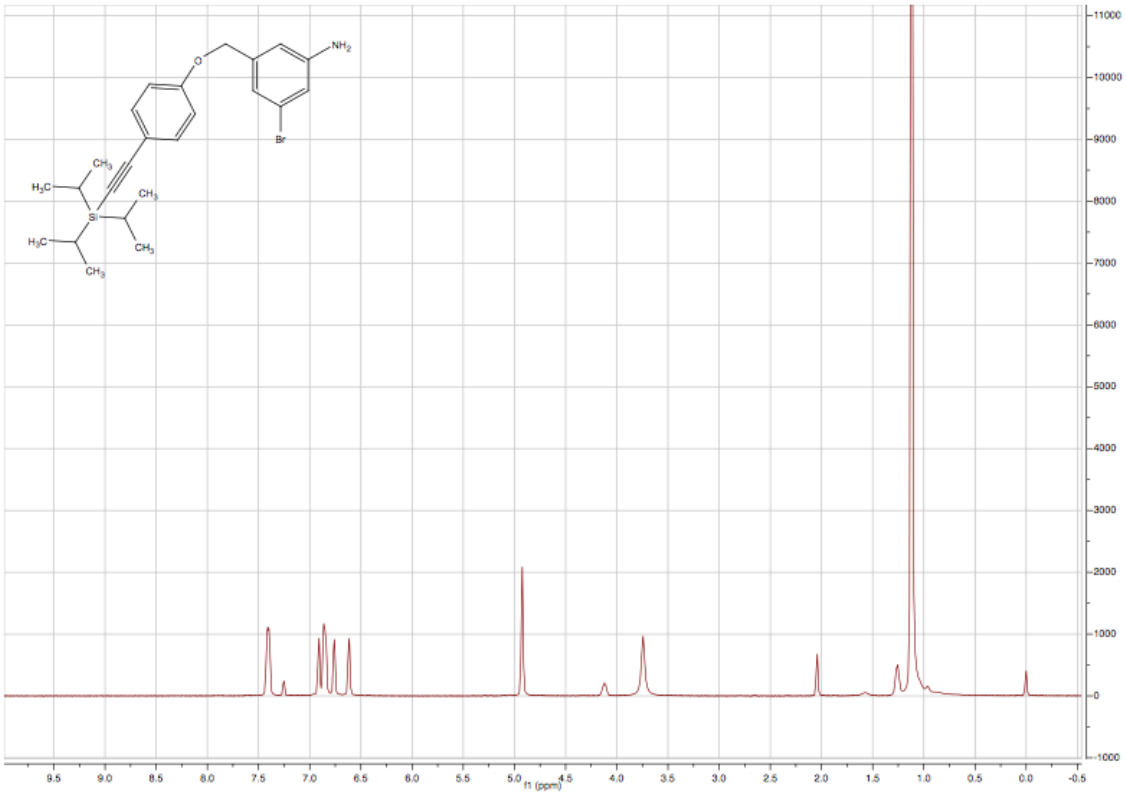


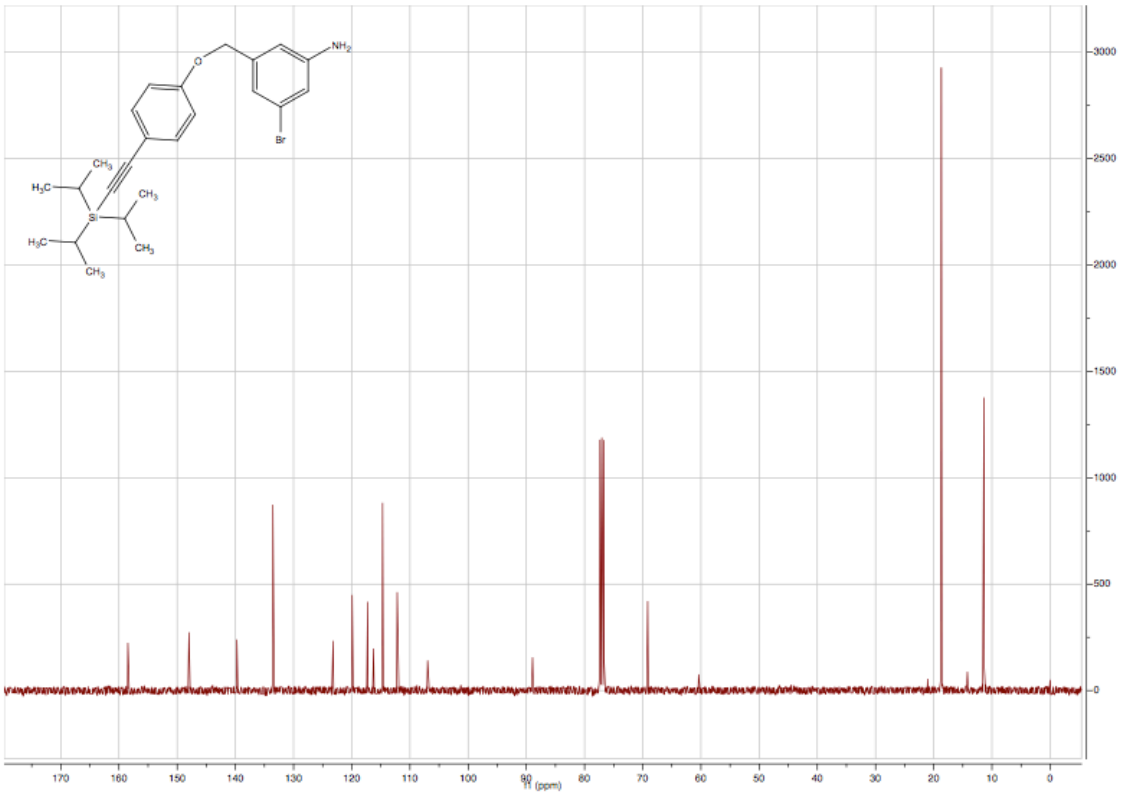
*{(4-[(3-Bromo-5-nitrobenzyl)oxy]phenyl)ethynyl}tri*isopropylsilane



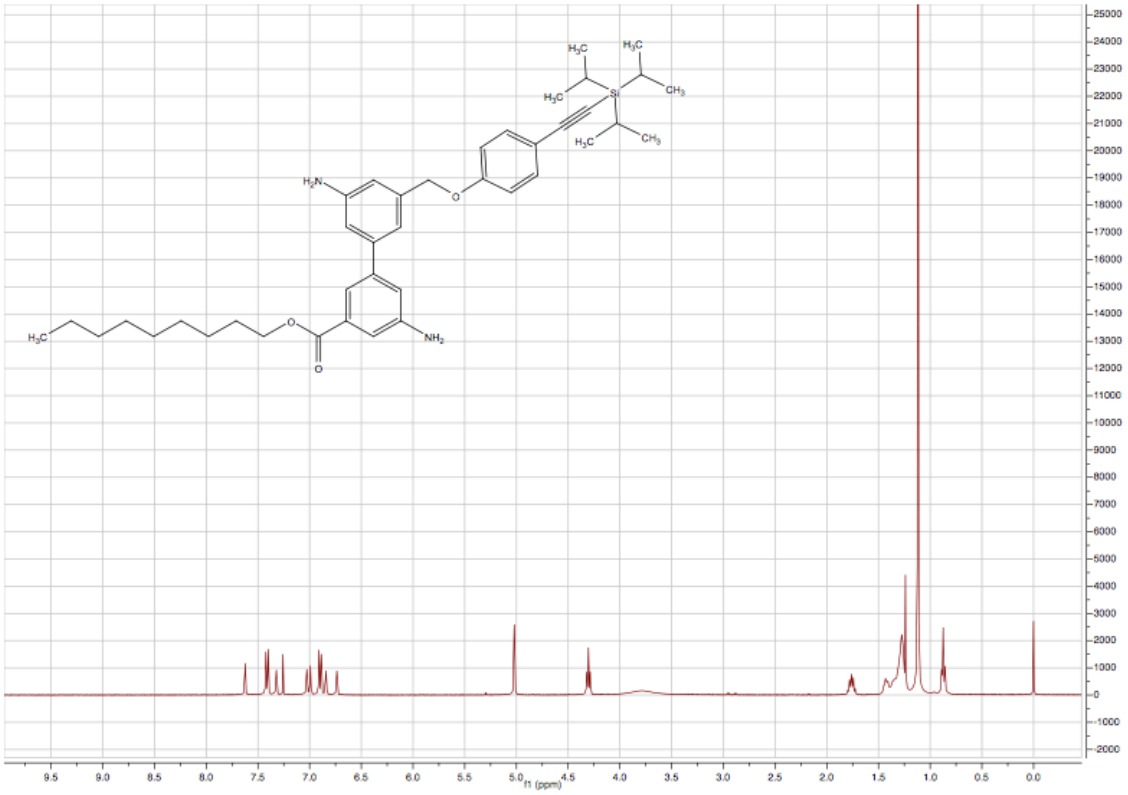


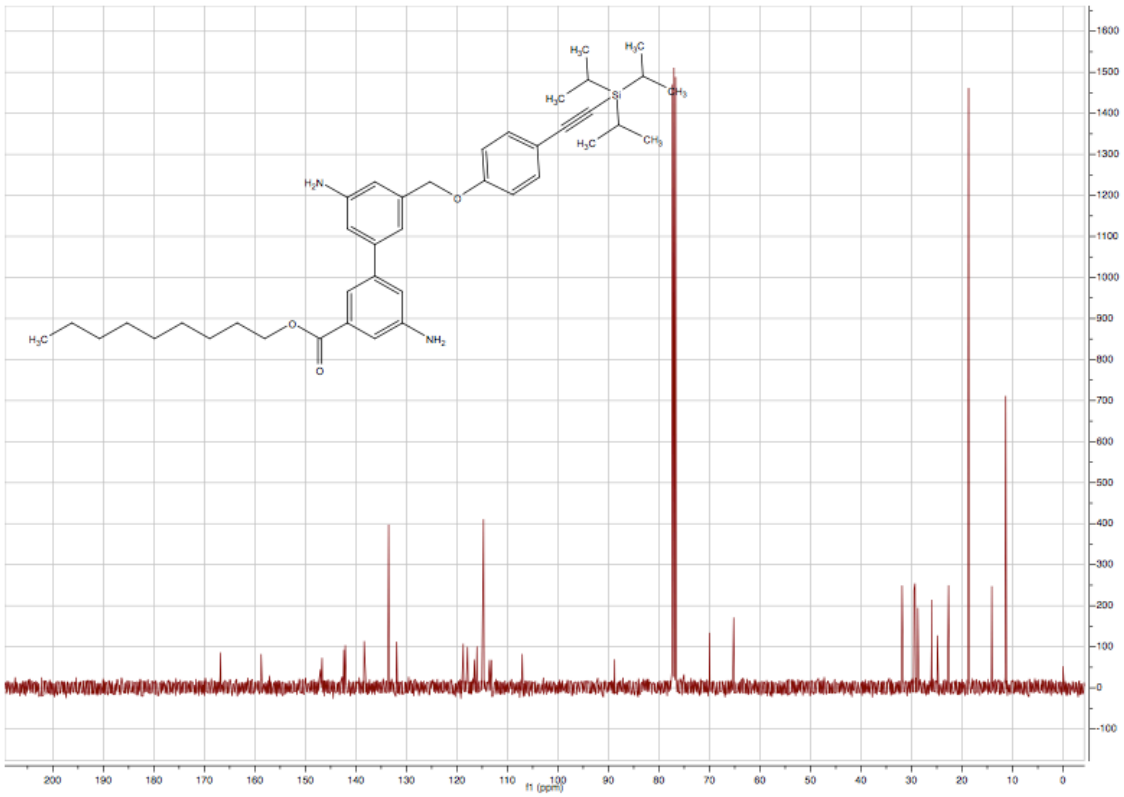
*3-Bromo-5-{(4-[(tri*isopropylsilyl)ethynyl]phenoxy)methyl}aniline



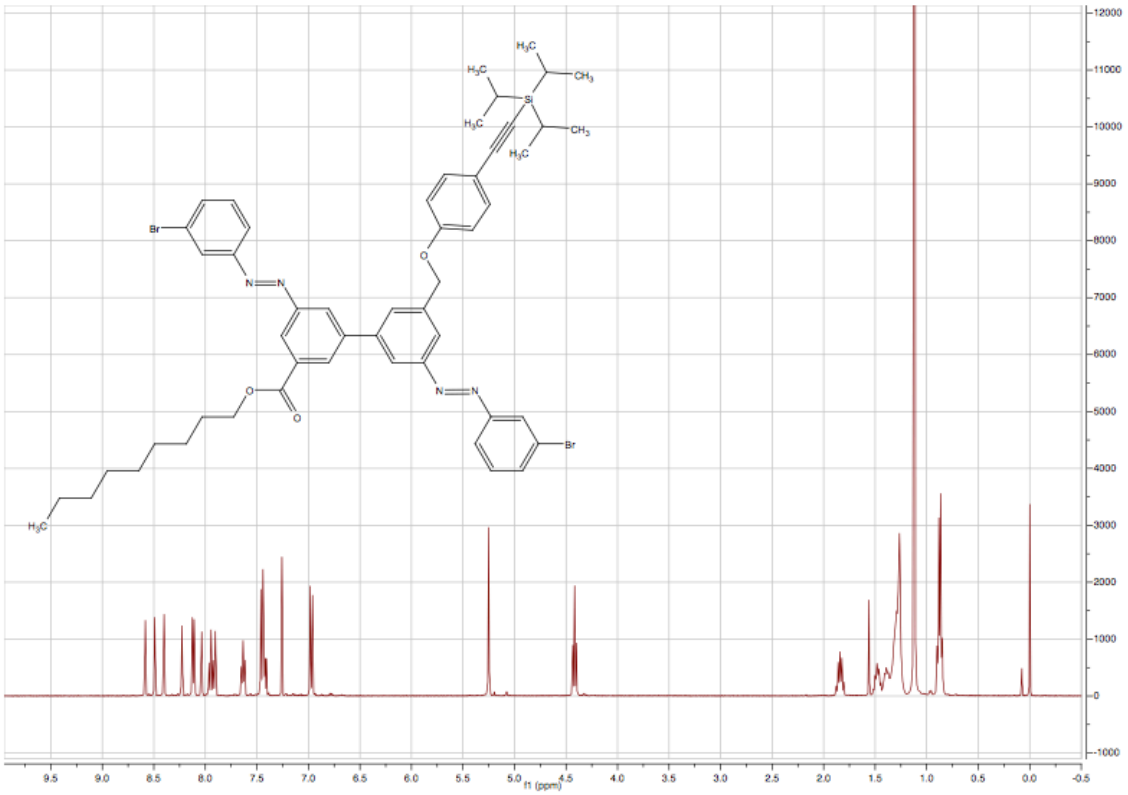


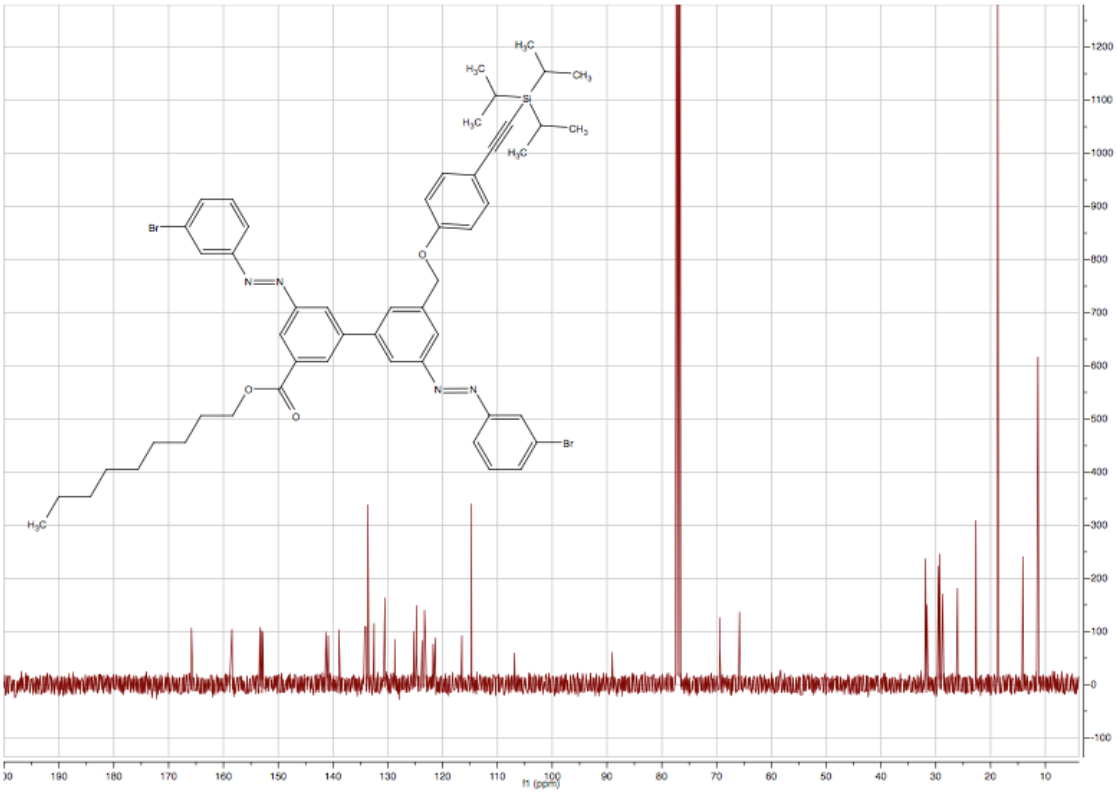
Diamine ***14***



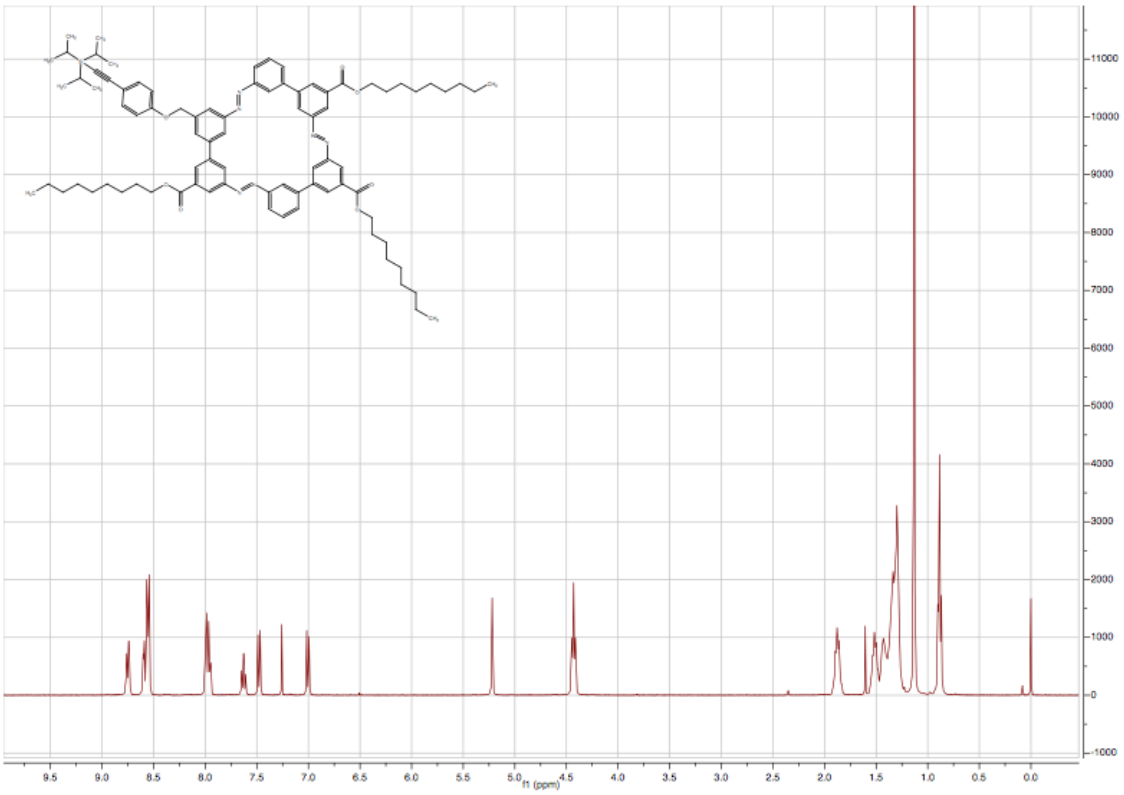


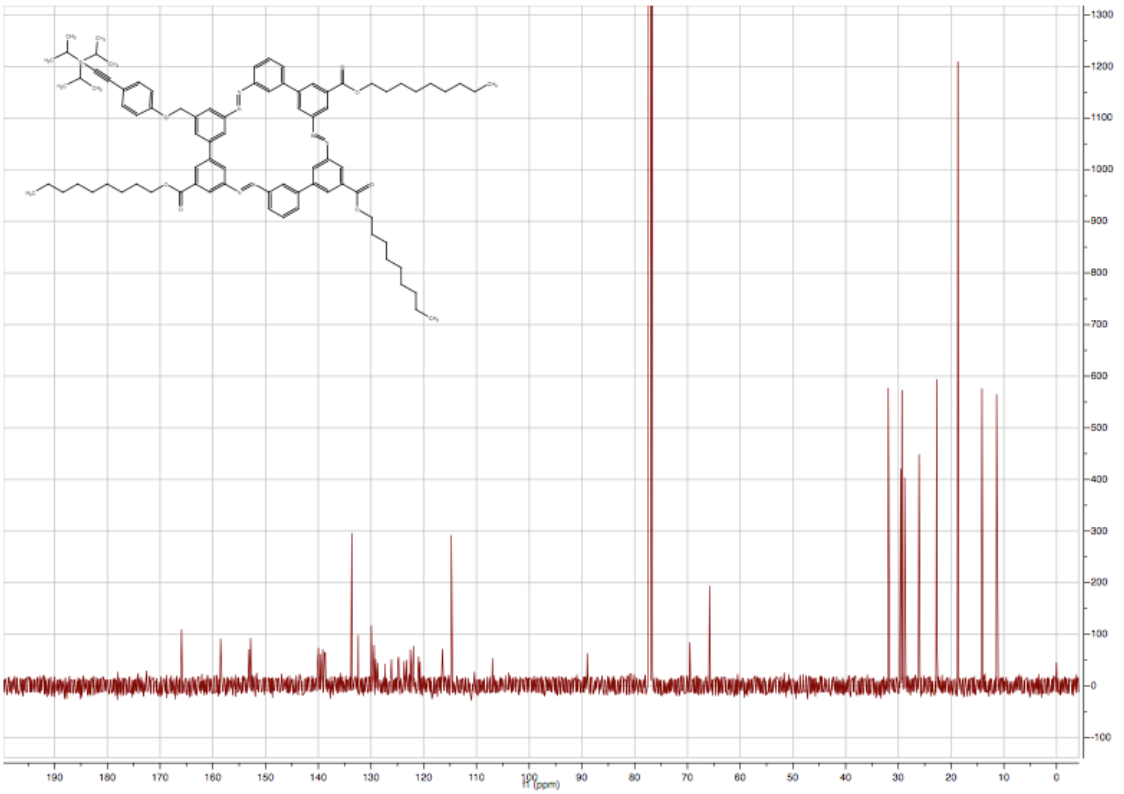
*Nonyl-3',5-bis[(*E*)-(3-bromophenyl)diazenyl]-5'-{(4-[(tri*iso*propylsilyl)ethynyl]phenoxy)-methyl}-[1,1'-biphenyl]-3-carboxylate*



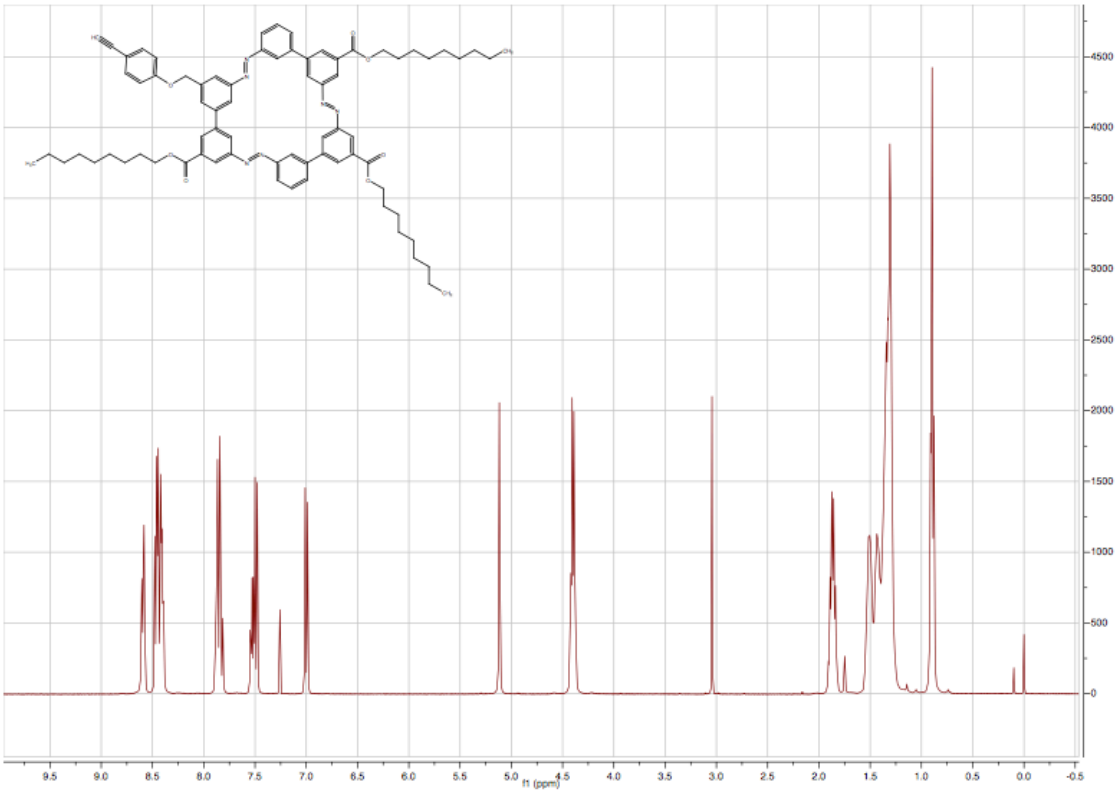


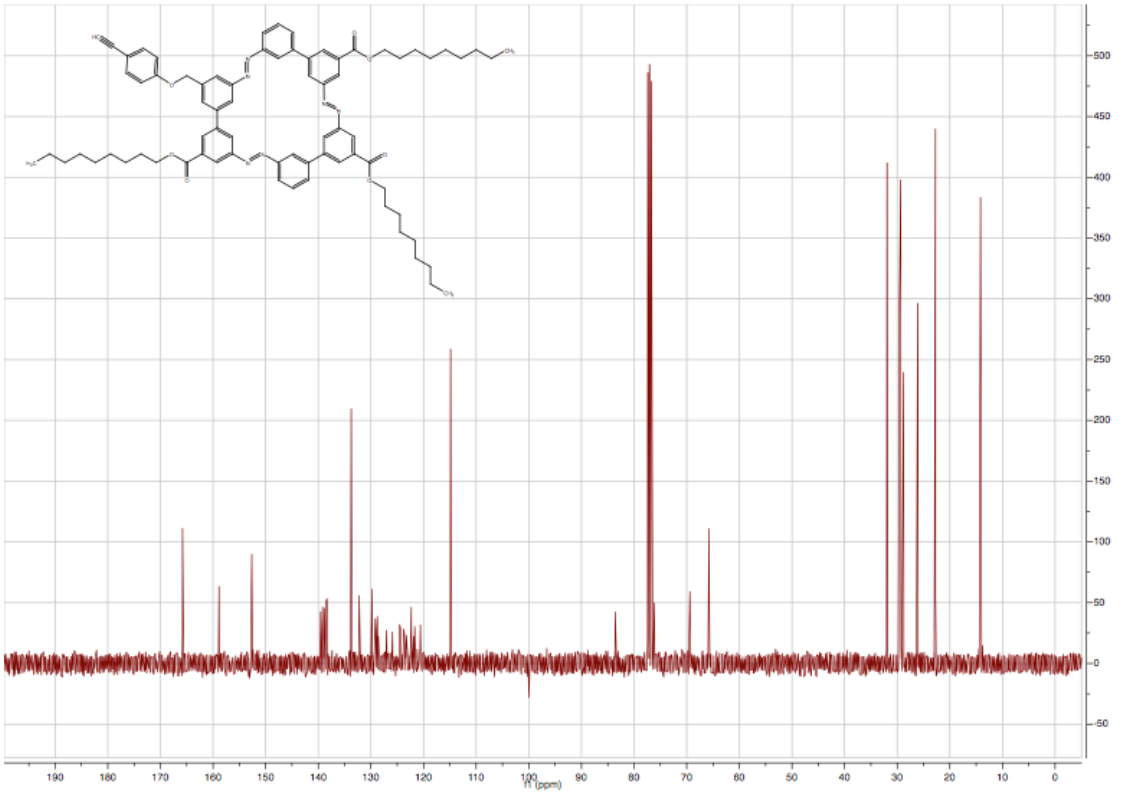
([(Triisopropylsilyl)ethynyl]phenoxy)methyl-macrocycle



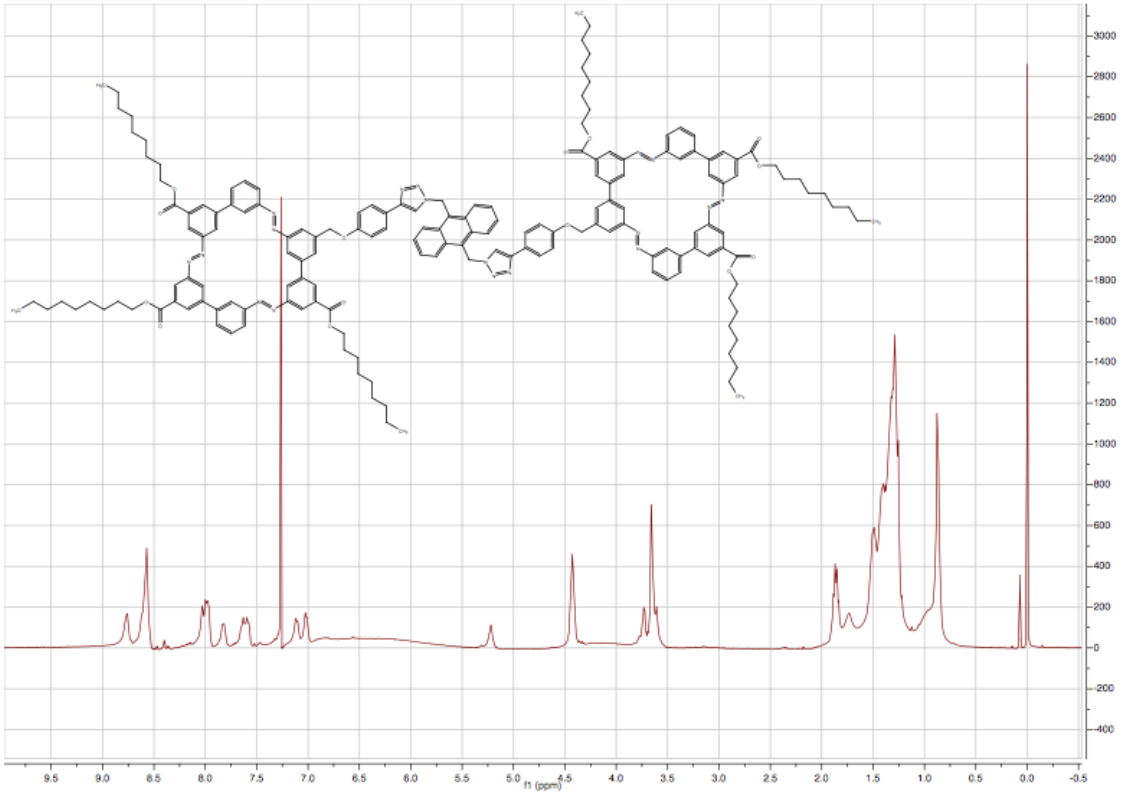


Macrocycle **15**

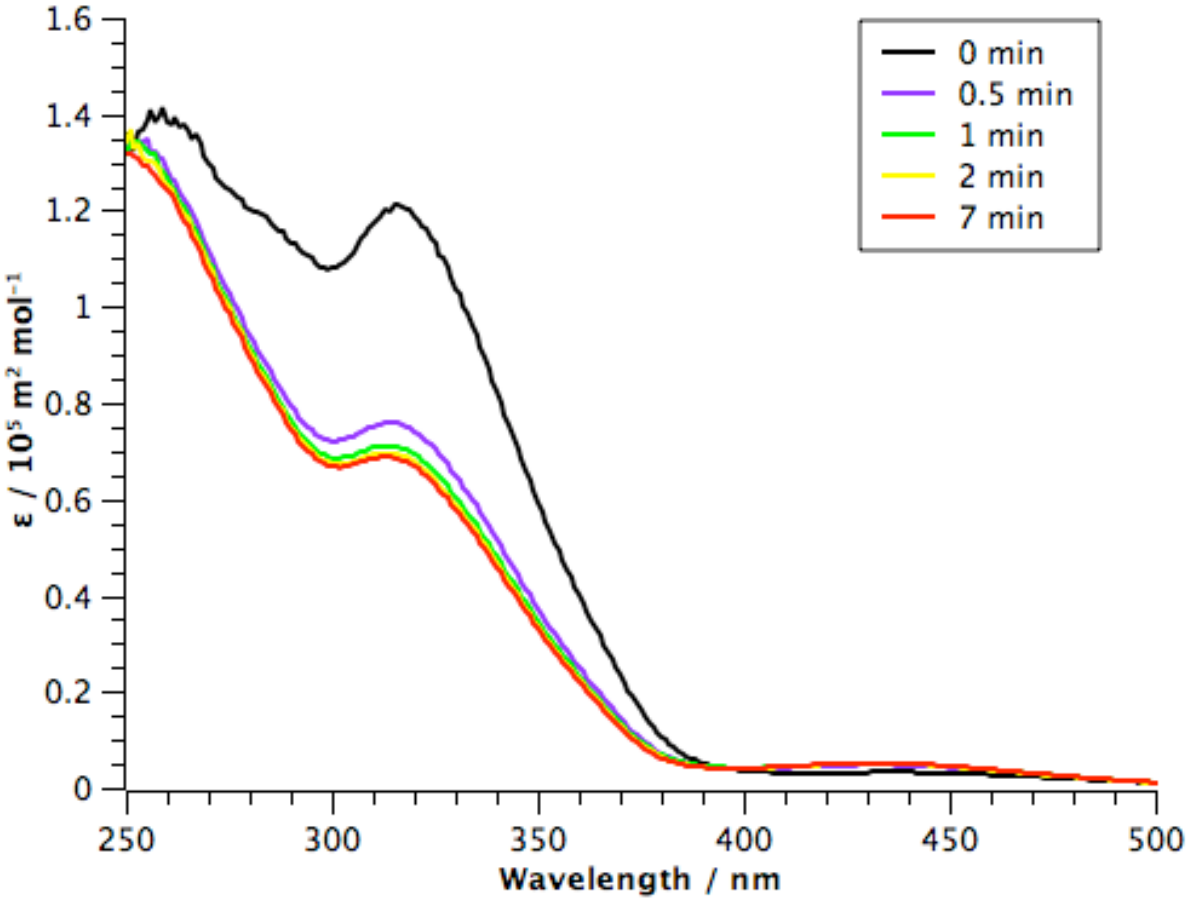




Bismacrocycle ***17***



UV spectrum of isomerization of macrocycle 1:



Photoswitching of macrocycle **1** (in $CHCl_3$, irradiation at 365 nm).

References:

[1] K. Rajesh, M. Somasundaram, R. Saiganesh, and K. K. Balasubramanian, *J. Org. Chem*., 2007, **72**, 5867.
[2] S. Lahiri, J. L. Thompson and J. S. Moore, *J. Am. Chem. Soc*., 2000, **122**, 11315.
[3] S. V. Aathimanikandan, B. S. Sandanaraj, C. G. Arges, C. J. Bardeen and S. Thayumanavan, *Org. Lett*., 2005, **7**, 2809.